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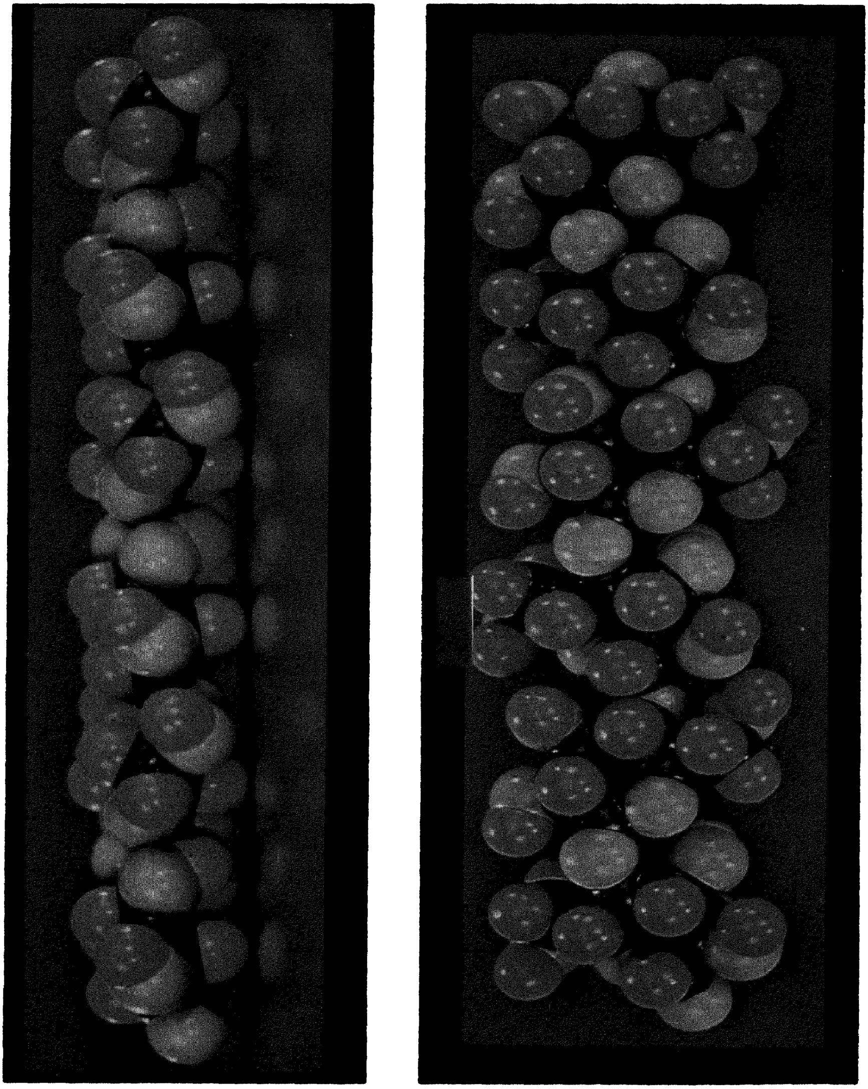

Side View

Top View

Cellulose Atom Model
Six units of the molecular chain

CELLULOSE AND CELLULOSE DERIVATIVES

Second Completely Revised and Augmented Edition

Prepared under the Editorship of
EMIL OTT HAROLD M. SPURLIN
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Research Department, Hercules Powder Company
Wilmington, Delaware

PART I

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PREFACE

When the first edition of this book was completed in 1943, the editors felt that knowledge in the cellulose field had reached a point permitting a definitive treatment of the subject. To a considerable extent this feeling has been substantiated. Facts and concepts outlined in the first edition have stood the test of time. With the passage of more than ten years, however, marked development has occurred in fundamental concepts, and sufficient new experimental data have accumulated to justify a complete reworking of the first edition.

Some new authors are encountered in this second edition because of the new type of emphasis and modification in arrangement of material necessitated by these modern developments. Other new contributors appear because some first-edition authors had changed their interests, or were prevented by other commitments from undertaking revisions of their earlier sections. To all authors contributing to this second edition, the editors would like to express appreciation for their genuine efforts and indispensable cooperation which have resulted in an almost completely new book rather than a mere revision of the earlier book.

The second edition, like the 1943 edition, aims "to present the most important modern scientific and technical information concerning cellulose and its derivatives." The revision brings up to date the original material and presents current thinking in the field. A major part of the book has been rewritten and there has been considerable reorganization of the contents. Scientific aspects are treated in full, and technological details and processing information are included to assist in a full understanding of materials in commercial use.

The effects of increased knowledge and new viewpoints since the earlier edition are especially evident in the chapters on fiber structure and mechanical properties, the more complete coverage of degradation of cellulose and its derivatives, and the expansion of the generalized and interpretative sections. Reorganization has resulted in better integration of the material on the pulp and paper industries and on substances associated with cellulose in nature. An introductory chapter to highlight the importance of cellulose and to justify the organization of the book has been added. Other new features include a chapter on tests and an appendix. The former contains a critical evaluation of available tests and methods of analysis for cellulose and its derivatives. The appendix contains charts showing relationships between degree of substitution and per cent of substituent, and between viscosity and concentration, temperature, and molecular weight. Comparative data on commercial products, a glossary of trade names, and similar information are also included.

For a work with the scope and character of this one, it was necessary, as for the earlier volume, to enlist the help of many authors. Then and now the editors recognized the inherent difficulties of a collaborative project. These have been minimized by the cooperative spirit of the authors. During the several years this project has been in progress, those authors whose manuscripts came in early have been exceptionally vigilant in incorporating pertinent latest information as it became available. The editors have also received constructive cooperation from all authors in making suggested changes to integrate the individual communications.

World conditions in the early forties necessitated the choice of authors residing in the United States. Although these conditions no longer exist, the editors were so satisfied with the earlier policy of working with authors with whom they could easily communicate and discuss the progress of their work, that for this edition no effort was made to locate authors outside the North American continent.

To assure the reader that the material presented in this book is not in conflict with the mass of confidential information possessed by all large industries, the editors have again followed the policy of drawing heavily on authors directly connected with industrial work in the cellulose field. These writers, who have access not only to knowledge possessed by industry but also to much of that contributed by academic and research institutions, are obviously in a good position to make certain that no commercially important factors are overlooked. Representatives of academic and research institutions comprise about one-fourth of the authors, however, to provide balance among viewpoints and because of the more fundamental nature of their contributions. The editors are convinced that the concerted efforts of these authors will contribute to future developments in cellulose chemistry and technology and that this new volume will become a valuable reference work in cellulose literature.

A number of colleagues of the editors also contributed substantially to the project. Dr. Peter VanWyck freely shared knowledge from his vast industrial experience in the cellulose pulping and paper fields and helped with the over-all planning and contacts with some prospective authors. Drs. James W. Davis, Vernon R. Grassie, Robert S. Voris, and P. Burke Welldon augmented the ranks of Hercules authors to constitute the editors' board of critical reviewers for all manuscripts. Miss Esther M. Coffin (now Mrs. A. F. Martin) and then Miss Leah Chandler have been capable and hard-working editorial assistants. Mr. S. V. Spoor and Mr. E. G. Weatherlow gave generously of their photographic and drawing talents to produce excellent copy for many of the illustrations.

It is a pleasant duty and privilege to express sincere thanks to these co-workers. Thanks are also due to Hercules Powder Company for continued interest in this project.

EMIL OTT
HAROLD M. SPURLIN
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Wilmington, Delaware
April, 1954

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CELLULOSE AND CELLULOSE DERIVATIVES

Part I

Chapter I

INTRODUCTION

EMIL OTT AND H. G. TENNENT

Cellulose is the most abundant and widely used organic chemical in the world. As the major constituent of plant matter, billions of tons of it are created each year through photosynthesis. In the form of wood, paper, cotton textiles, rayon, film, plastics, coatings, and a myriad of other uses including fuel, man consumes throughout the world about 450,000,000 tons of cellulose per year. This compares with annual world consumptions of about 180,000,000 tons of steel, 1,400,000,000 tons of coal, 500,000,000 tons of petroleum, 500,000,000 tons of cereals, and 36,000,000 tons of sugar.

Naturally this basically important material has been the subject of an enormous amount of investigation. Studies of its occurrence, formation, isolation and purification, chemical and physical structures, properties, reactions, and uses have led to considerable understanding of its nature and behavior. In fact, studies leading to recognition of the polymeric nature of cellulose were among the first on polymers of any sort, and many of the basic principles of polymer chemistry were worked out in the course of cellulose investigations. These principles contributed to the understanding of the behavior of the other two important classes of naturally occurring polymers, proteins and rubber, and they have been the basis for the development of the numerous and rapidly growing family of synthetic polymers.

The purpose of this book is to describe the most important features of the chemistry and chemical technology of cellulose and its derivatives. The emphasis on the chemical features of cellulose behavior requires the omission of several important parts of the total cellulose technology, notably the manufacture of textiles from natural or man-made fibers, the conversion of wood to lumber and its use as such, the technology of making and finishing many kinds of paper, the spinning of cellulose acetate fibers, and the principles involved in the formulation and use of nitrocellulose lacquers and explosives. The operations in these fields are primarily physical, rather than chemical. Even with these large omissions, however, there is so much material which might be covered that selection of topics has been necessary to keep the size of the book reasonable. The purpose of this introductory chapter is to provide perspective for the more detailed chapters which follow, and to clarify for those not familiar with cellulose technology the reasons for including some of the topics whose importance may not be self-evident.

Several editorial principles should be mentioned at this point. For brevity and clarity, in this book subjects are described more as they stand today than as they developed historically. This results in the omission of much documentary material of real interest but of secondary importance in understanding the subjects discussed. On the other hand, each chapter has been written to be largely self contained, even at the expense of some repetition of material elsewhere in the book. This is necessary because the same physical and chemical factors play an important role in several different aspects of cellulose behavior. Also, the increase in the book's reference value warrants this repetition.

In several of the chapters, hypotheses and interpretations are stressed as much as or more so than purely factual matter. These are not all universally accepted as yet, and may subsequently have to be changed in some respects as new facts are found. Nevertheless, they have been included because they do rest on an increasingly broad factual base and because they contribute so much to correlating and understanding the many facts which are known. The goal is a unified, self-consistent, relatively simple explanation of the behavior of cellulose. Since issuance of the first edition of this book, there has been significant progress toward this goal, especially in understanding the structure and chemical reactivity of cellulose fibers. It is not unlikely that the hypotheses and interpretations assembled in the first edition may have contributed to this progress. In this hope, and because the picture is becoming ever clearer, interpretative material is emphasized in some parts of this edition even more than it was in the first edition.

In a number of cases, alternative explanations of some observations have been advanced in the literature. In many instances not enough facts are yet available to prove which are correct. In such cases, the explanations have been favored which require the fewest special assumptions and which depend only on principles which have been well established in other simpler fields of chemistry. The history of science and of the development of cellulose chemistry supports this policy. Several theories invoking long-range forces, special micellar structures, or other unusual effects have enjoyed wide acceptance at various times, yet all have been supplanted by explanations involving only ordinary chemical and physical principles. It seems reasonable to believe that such simple explanations should always be possible, and it must be the aim of all science to reduce the abundance of facts to the simplest explanations and correlations.

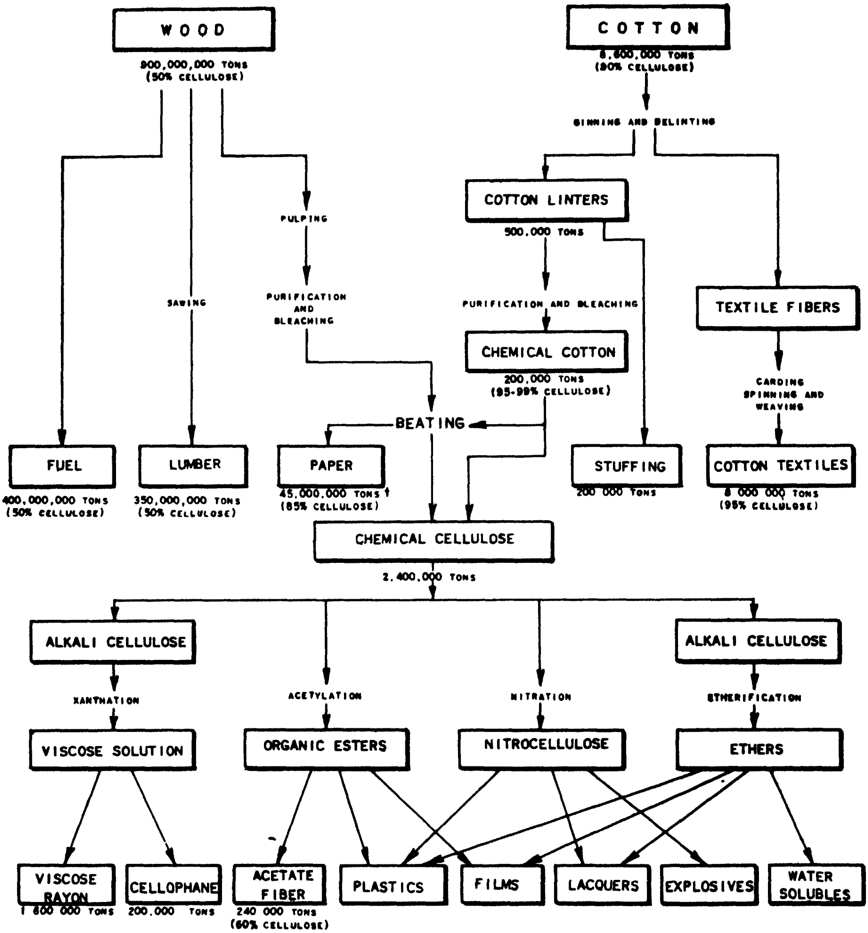
CELLULOSE TECHNOLOGY

The flow of cellulose from its commercially important sources through various converting operations into its chief end uses is shown in Figure 1. Annual volumes cited are estimates based on the best figures available, and are intended primarily to show the relative importances of the various operations and uses. They should not be considered or used as correct absolute figures, since completely accurate data are not available in all cases.

It can be seen that there are two main commercial sources of cellulose: wood and cotton seed hairs. Though cellulose may be derived from many other vegetable sources, the original cost, difficulties in collection, problems in its isolation from noncellulosic materials also present, or quality limitations to the cellulose finally obtained have kept these other sources relatively less important.

In lumber and in cotton textiles, cellulose is used essentially as it occurs in nature. In paper, cellulose fibers from wood, freed from lignin, are used with little further modification. Thus, the three major uses of cellulose take advantage of the strength and toughness of naturally occurring fibers, cemented with lignin in wood, twisted and woven together in textiles, matted and adhering to one another in paper.

In fact, cellulose almost never occurs in nature except in the form of fibers, though its fibrous nature is not always obvious. Since the fibers are not soluble in practical solvents, and since they decompose rather than melt on heating, they are not readily convertible to other shapes in which the inherent strength of cellulose could be used to advantage. However, large industries have developed based on chemical conversion of cellulose to soluble products from which cellulose is regenerated in new shapes. Viscose rayon and cellophane are the chief examples of this class, about 1,800,000 tons being made annually in the world. Another group of important industries is based on chemical conversion of cellulose to soluble or fusible derivatives which are then used as such after they have been shaped to the desired form. In this way, several physical properties are also desirably altered. Examples are acetate fibers, nitrocellulose coatings, and cellulose ester and ether plastics and films. World production of such derivatives is about 350,000 tons annually. The commercially


WOOD
900,000,000 TONS
(50% CELLULOSE)
COTTON
8,600,000 TONS
(90% CELLULOSE)
GINNING AND DELINTING
COTTON LINTERS
500,000 TONS
PULPING
SAWING
PURIFICATION AND BLEACHING
PURIFICATION AND BLEACHING
TEXTILE FIBERS
CHEMICAL COTTON
200,000 TONS
(95-99% CELLULOSE)
CARDING SPINNING AND WEAVING
BEATING
FUEL
400,000,000 TONS
(50% CELLULOSE)
LUMBER
350,000,000 TONS
(50% CELLULOSE)
PAPER
45,000,000 TONS †
(85% CELLULOSE)
STUFFING
200 000 TONS
COTTON TEXTILES
8 000 000 TONS
(95% CELLULOSE)
CHEMICAL CELLULOSE
2,400,000 TONS
ALKALI CELLULOSE
ALKALI CELLULOSE
XANTHATION
ACETYLATION
NITRATION
ETHERIFICATION
VISCOSE SOLUTION
ORGANIC ESTERS
NITROCELLULOSE
ETHERS
VISCOSE RAYON
1 800 000 TONS
CELLOPHANE
200,000 TONS
ACETATE FIBER
240 000 TONS
(60% CELLULOSE)
PLASTICS
FILMS
LACQUERS
EXPLOSIVES
WATER SOLUBLES

† *This figure includes some re-used cellulose; hence, the amount of new cellulose used is somewhat lower.*

Fig. 1. World cellulose use pattern. Quantities given are rounded-off estimates, and are included to indicate the approximate relative magnitudes of various uses. They should not be considered or used as correct absolute figures, since accurate data are not available in all cases. Sources used include: *Yearbook of Forest Products Statistics*, 1951 (Food and Agriculture Organization of the United Nations); *Statistical Yearbook 1949–1950* (United Nations); *Textile Organon*, June 1953 and March 1952 (Textile Economics Bureau, New York), *Pulp and Paper*—World Review Number, August 1953.

important chemical operations in making regenerated cellulose and cellulose derivatives are covered in considerable detail in Chapter IX.

The structure of wood has a profound influence on its properties as a construction material and on the ease with which the cellulose fibers in it may be separated from the noncellulosic constituents also present in roughly equal amount. The chief noncellulosic constituent is lignin, whose composition and chemistry are thus also very significant in winning cellulose from wood. Wood structure and lignin are described in Chapter V. Several methods of isolating cellulose from wood (pulping) have achieved commercial success and are the basis of very large industries, each involving complex chemistry and economic factors. The methods used and problems involved are the subject of Chapter VI.

Fibers separated from lignin are usually bleached and further purified to some extent. The greatest degree of purification is required for cellulose which is to be used for manufacture of chemical derivatives. Cellulose for most paper uses needs not be so pure, though paper quality (whiteness, strength, and retention of these on aging) improves with increasing purity. A complex and important technology has been developed for the bleaching and purification of cellulose for various purposes. It is discussed in Chapter VII.

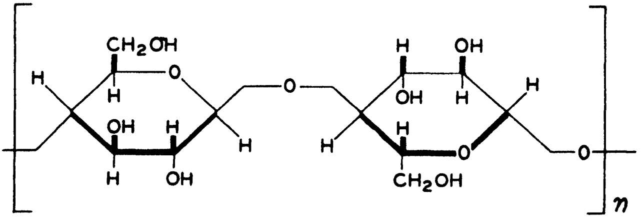
The fibers used to make paper are subjected to mechanical working in contact with water ("beating") to alter their surfaces to promote their adhesion to one another on drying in the final paper sheet. Though this is primarily a physical effect rather than chemical, knowledge of its characteristics is important to understanding variations in the subsequent behavior of the sheet in chemical reactions. Also, the bonding of fibers in paper gives insight into the bonding of fibrils to make the original natural fibers. Thus, the beating process is covered in considerable detail in this book (Chapter VIII).

CELLULOSE CHEMISTRY

It is not easy to give a chemical definition of the word "cellulose" which fits all the uses of the word. Nature and man's activities usually defy neat classifications, and both are involved in the definition of cellulose. Carbohydrates, along with other very different kinds of compounds, are synthesized by growing plants. The carbohydrates may be considered as derived from several simple monosaccharides, predominantly glucose. Some of the saccharide units may be chemically linked with noncarbohydrate compounds also present. Others may have been oxidized or chemically altered in other ways, so that functional groups are present which are not part of pure carbohydrates. To separate the various components of plants, chemical reactions must be used. These reactions inevitably alter the original materials to some extent, though usually only slightly. Thus a naturally occurring mixture of compounds is subjected to conditions which permit the formation of numerous derivatives. The resulting even more complex mixture may then be fractionated but never completely separated into pure compounds. The term "cellulose" is often applied to specific fractions isolated from the original plants in such a manner. When used in this way, the word has exact meaning only if the starting materials and the operations used to separate the fraction designated cellulose are specified and understood. In such cases, the term does not refer to a single chemical entity.

On the other hand, an idealized chemical entity can be defined and called "cellulose," though it may never have existed and may never be isolated. This ideal cellulose is the compound which actual fractions approach more closely, the more carefully they are isolated and purified. Discussions of theoretical principles are usually based on this ideal cellulose, whereas in technological discussions, "cellulose" usually refers to actual fractions obtained by the methods being discussed. Even the best methods yield products in which a fraction of one per cent of the components are different from the ideal or theoretically perfect cellulose. One should always bear in mind, however, that experimentally observed facts are necessarily obtained from actual, not theoretical, cellulose, and may be conditioned by the deviation from the ideal.

The "ideal" cellulose is a linear polymer composed of individual anhydroglucose units (also called glucopyranose units) linked at the 1 and 4 positions through glucosidic bonds with the beta configuration. Thus, it has the following repeating unit, with *n* having values ranging from about



50 to 5000 or more. Although this structural formula explains much of the behavior of cellulose, it should be supplemented by the scale model, two views of which are shown in the Frontispiece. (In this model, carbon atoms are black, oxygen are blue, and hydrogen are orange. The small size of the anhydroglucose ring, the relative bulk and positioning of the

—CH_2OH and —OH groups, and the angle of the rotatable —C—O—C— bond between anhydroglucose units become clearer in this model.)

Although many cellulose properties are readily explainable on the basis of its molecular formula, others are not. In many of the latter cases, this is because the behavior of cellulose is modified by the nature of its solid state. It is neither completely crystalline like glucose, nor amorphous like a supercooled liquid but has some aspects of both states. The crystallizing tendency inherent in such regular and highly polar units as the anhydroglucose rings is counteracted by the difficulty of getting the rings in regular crystalline array because they are parts of long, somewhat flexible, mutually entangled chains. As a result, no two cellulose fibers have exactly the same internal structures; each reflects its individual history. This internal structure is important, since it profoundly affects both the useful strength properties of the fibers and the rate and extent to which the cellulose in them reacts with other reagents. It governs chemical reactions by limiting the access of reagents to the cellulose molecules within the solid. Because of this limited accessibility, many reactions which proceed rapidly with glucose do not occur to a measurable extent with cellulose under the same conditions. A vital part of the technology of making cellulose derivatives is the art of providing conditions such that all parts of the cellulose to be reacted are readily accessible. Failure to do so results in nonuniform products with poor clarity, solubility, filterability, and flow characteristics in solutions and moldings. Because of the importance of cellulose internal structure to reactivity and properties, much work has been done to understand the nature of the solid state of cellulose, to measure variations, and to relate these variations to behavior. The field is still very active, and much remains to be done. Much of the content in Chapter IV (Structure and Properties of Cellulose Fibers) is the result of studies of these problems.

The good mechanical properties (strength) of cellulose and derivatives, on which their utility depends, is due to their polymeric nature. The conditions of use and of conversion of cellulose to derivatives are often conducive to depolymerization with consequent loss of such strength. Weathering, laundering, oxidation, and acid and alkaline reactions can produce this effect. In many uses, an optimum degree of polymerization (D.P.) exists because of the necessity of balancing strength against ease of flow in solution or melts. Ease of flow is required for fabrication operations and is favored by low D.P., whereas strength is favored by high D.P. The best compromise is usually well below the D.P. of natural cellulose, and must be achieved by controlled depolymerization. For these reasons, the depolymerization and degradation of cellulose and its derivatives is of great practical importance and has been studied extensively. Section C of Chapter III and Section G of Chapter IX discuss some of this work.

The stability and reactivity of cellulose, and the color, clarity, filterability in solution, and stability of its derivatives are strongly dependent on the kind and amount of impurities associated with them. The practical importance of these properties has led to a highly developed technology of cellulose purification and extensive study of the nature of common impurities. Since cellulose is polymeric, it cannot be purified by recrystallization like sugar, nor by distillation of monomers before polymerization. The impurities must be removed by extraction, with or without previous chemical modification. Chapters V and VII cover these topics.

Much of our understanding of the polymeric nature of cellulose and its derivatives comes from a study of the properties of their solutions. Solution viscosity measurements offer the most convenient means of estimating and controlling the degree of polymerization of cellulose during processing. Fabrication of fibers, sheets, and coatings from cellulose derivatives most frequently entails rapid deformation of their concentrated and, hence, highly viscous solutions. Formulated cellulosic plastics, films, and coatings are usually plasticized with high-boiling liquids which act as permanent solvents. In many ways, therefore, the nature of polymer–solvent interactions and the properties of cellulose and cellulose derivative solutions have theoretical and practical importance, and a good deal is known about them. Much of this knowledge is applicable to other polymers as well. Chapter X is devoted to this subject.

Cellulose and cellulose derivatives are useful and important primarily because of their strength, toughness, and flexibility. The purpose of chemical and physical treatments of these materials is to prepare a final product which has these good properties. Hence, a discussion of the mechanical properties which may be realized from cellulosics is given in Chapter XI. This supplements and extends the material in Chapter IV (fibers) and in Chapter X (solutions), and makes use of the subjects of molecular weight and degradation covered in Chapter III (chemical nature).

To summarize, cellulose is a material of transcendant interest because of its widespread natural occurrence and its past and present practical importance. Scientific curiosity and technological necessity have led to a great deal of knowledge about it. Perspective is required to assess the relative importance of the parts of this knowledge. The parts covered in this book have been selected on the basis of their general interest, importance, and applicability to a wide variety of problems in cellulose chemistry and chemical technology. It is hoped that they will prove useful to those seeking to extend still further our knowledge of this field.

Chapter II

OCCURRENCE OF CELLULOSE

KYLE WARD, JR.

Cellulose is the most abundant of all naturally occurring organic compounds and probably makes up at least a third of all the vegetable matter in the world. It is the main constituent of the cell walls of the higher plants, having received its name for this reason.[1] Its existence in the lower orders of the vegetable kingdom has been disputed, but there is good evidence that it does occur in many of the lower species.

For instance, cellulose has been reported absent in the tubercle bacillus[2] and in several other bacteria.[3] The microscopical evidence of Farr and Eckerson[4] indicates its presence, however, in *Acetobacter xylinum*, and in the cellulosic membrane produced by this organism it has been identified[5] by all the better known techniques, including the x-ray diffraction pattern and acetolysis to cellobiose octaacetate.

Similarly, cellulose has been reported absent or present only in very small amounts in the algae, fungi, and lichens.[6] It has been identified in *Laminaria digitata*, however, by the formation of methyl and acetyl cellulose, by the viscose reaction, and by the hydrolysis to glucose.[7] As a result of the last reaction, as well as from a study of pyrolysis products, cellulose has been reported[8] in two other species of *Laminaria* and two of *Fucus*, including the same species studied in the negative report just cited.[6] Miwa[9] reports that cellulose is lacking in *Porphyra*, but constitutes 5 to 15%

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[1] A. Payen, *Compt. rend.*, **7**, 1052, 1125 (1838).

[2] O. Binder, *Compt. rend.*, **197**, 197 (1933).

[3] C. van Wisselingh, *Pharm. Weekblad*, **53**, 1069, 1102 (1916); through *Chem. Abstracts*, **10**, 3090 (1916).

[4] W. K. Farr and S. H. Eckerson, *Contribs. Boyce Thompson Inst.*, **6**, 189 (1934).

[5] H. Hibbert and J. Barsha, *Can. J. Research*, **5**, 580 (1931).

[6] R. S. Hilpert, D. Becker, and W. Rossee, *Biochem. Z.*, **289**, 179 (1937).

[7] T. Dillon and T. O'Tuama, *Sci. Proc. Roy. Dublin Soc.*, **21**, 147 (1935); through *Chem. Abstracts*, **29**, 2735 (1935).

[8] G. Viel, *Compt. rend.*, **208**, 532 (1939).

[9] T. Miwa, *Japan. J. Botany*, **11** (1), 41 (1940); through *Biol. Abstracts*, **16**, 499 (Abstract No. 5517) (1942).

of most brown algae and 1.5 to 3% of the Florideae. Particularly convincing evidence of the presence of cellulose in *L. Cloustoni*, *L. digitata*, and *F. vesiculosus*, including acetolysis data and x-ray diagrams, was obtained by Percival and Ross.[10] In this connection it should be pointed out that the structural material in marine algae is sufficiently similar to cellulose that its use in paper pulp has been seriously considered.[11–13] Cellulose has been reported in yeast, the identification consisting of insolubility in alkali and hydrolysis to glucose.[14] By means of staining reactions, cellulose was identified in the lower fungi in the Oömycetes and in a new species, *Rhizidiomycetes bivellatus*, among the Chytridiaceae. No cellulose was found in other Chytridiaceae, Blastocladiaceae, Ascomycetes,[15] or Actinomycetales.[16]

Among the mosses and ferns, cellulose has been quite definitely identified in brake fern[17] and in hair cap moss,[18] the formation of cellobiose octaacetate serving as evidence. The same investigators, using the same criteria,[19] have also established the presence of cellulose in Spanish moss, which is not a true moss.

These references by no means cover the field of cellulose in the lower plants. They merely cite examples showing how well authenticated its existence is in certain cases. Where the less specific microchemical tests of the botanist are used as criteria, cellulose is reported from nearly every type of vegetable life.

As an example, the presence of cellulose, indicated by the sulfuric acid-iodine test, has been reported[20] in plants from four families of fungi (in stipes, gills, basidiospores, sporangiophores, mycelia, and spores), from twenty families of algae (in cell walls and cytoplasm), from two families of liverworts (in rhizoids, thalli, gemmae, spore mother cells, and tetrads), from three families of mosses (in leaves, paraphyses, spores, and stems), and from three families, ten species of pteridophytes (in spores, sporangia, prothalli, rhizoids, epidermal hairs, leaves, and roots). Fifty species of the higher plants, well distributed throughout the various divisions of the spermatophytes, were also investigated. The tissues investigated in the spermatophytes were from all parts of the plant-root, stem, leaf, flower, and fruit; they included such differentiated materials as cell walls, epidermis, hairs, cortex, wood, bast fibers, buds, coleoptiles, petioles, veins, corn silk, anthers, pollen, calyxes, pistils, corollas, peduncles, husks, and seeds.

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[10] E. G. V. Percival and A. G. Ross, *Nature*, **162**, 895 (1948); *J. Chem. Soc.*, **1949**, 3041.

[11] V. Hottenroth, *Papier-Fabr.*, **32**, Tech.-wiss. Tl., 337 (1934).

[12] V. de Buen, *Rev. ing. ind.*, **1**, No. 6, 5; No. 8, 12 (1930); through *Chem. Abstracts*, **25**, 1937 (1931).

[13] T. Dillon, D. T. Flood, V. C. Barry, and P. O'Muineacáin, Brit. Patent 508,671 (July 4, 1939).

[14] E. Salkowski, *Z. physiol. Chem.*, **114**, 31 (1921).

[15] K. Nabel, *Arch. Mikrobiol.*, **10**, 515 (1939); through *Chem. Abstracts*, **35**, 5147 (1941).

[16] O. V. Plotho, *Arch. Mikrobiol.*, **11**, 33 (1940); through *Chem. Abstracts*, **35**, 5147 (1941).

[17] W. M. Harlow and L. E. Wise, *Am. J. Botany*, **25**, 217 (1938).

[18] W. M. Harlow and L. E. Wise, *Am. J. Botany*, **25**, 760 (1938).

[19] L. E. Wise and A. Meer, *Proc. Florida Acad. Sci.*, **1**, 131 (1936); through *Chem. Abstracts*, **32**, 2984 (1938).

[20] F. L. Barrows, *Contribs. Boyce Thompson Inst.*, **11**, 61 (1939).

A. SIGNIFICANCE OF TERMS

The word "cellulose," when used in a technological sense, does not mean exactly the same thing as when used to denote an organic compound. Technologically, "cellulose" denotes the residues obtained by subjecting vegetable materials to certain pulping processes. These pulps consist mainly of cellulose and closely related materials, but may differ both in amount and nature of the noncellulosic constituents. The content of cellulose varies with the pulping process and with the material used. Cellulose, in the chemical sense, is a polysaccharide of sufficient chain length to be insoluble in water or dilute acids and alkalies at ordinary temperatures, consisting of anhydroglucose units linked together through the 1 and 4 carbon atoms with a β-glucosidic linkage, and giving a typical x-ray diagram. The possibility of the occurrence of other sugar units or other linkages has often been suggested, but experimental evidence for any particular irregularity is scanty. The subject will be treated in the next chapter (III-B). See also the report by Huggins, *et al.*[20a]

Even if the definition just given is accepted as accurate, it does not mean that cellulose consists of identical molecules, as do the compounds of lower molecular weight. The number of anhydroglucose units per molecule may vary over a wide range. A given sample of cellulose will thus contain many molecules of different lengths. The so-called degree of polymerization represents an average value for the number of anhydroglucose units in the molecule. The natural celluloses have a degree of polymerization of several thousand[21]; the highest value obtained by viscometric methods is 15,000,[22] but hydrolyzed material may drop into the so-called "mesocolloid" range, 50–500, and still retain the characteristics of cellulose. The methods of determination of degree of polymerization and the discrepancies between methods will be discussed in Chapter X-D.

[20a] M. L. Huggins, *et al.*, *J. Polymer Sci.*, **8**, 257 (1952).

[21] E. Heuser and L. Jörgensen, *Tappi*, **34**, 57 (1951).

The differences between cellulosic pulps from different sources may be due to differences in the structure of the cellulose present, but it appears more probable that these differences are due largely to differences in the noncellulosic ingredients, in the degree of polymerization of the cellulose, and in the physical structure of the individual fibers. Fibers from different sources have markedly different structure (see Chapter IV-C).

Alpha-cellulose refers to that portion of industrial cellulose pulps which is insoluble in cold sodium hydroxide of mercerizing strength (17.5 or 18%). Beta-cellulose is soluble in such a solution but is precipitated on acidification, while gamma-cellulose remains in solution on acidification. Beta- and gamma-celluloses are not necessarily true celluloses in the sense that they contain only polymers of anhydroglucose units. They may consist of polymers of other sugars such as the xylans, oxidation products such as oxycellulose, or true cellulose compounds of low molecular weight. The alpha-cellulose fraction, from whatever source derived, probably consists to a very large extent of cellulose as just defined. Algar, Giertz, and Gustafsson,[23] have suggested that beta-cellulose in wood pulps is essentially degraded alpha-cellulose not existing in the wood but produced during pulping and that gamma-cellulose is essentially hemicelluloses. While not universally accepted, this generalization has been confirmed by several other workers.[23,23a–c] There are a number of methods, both gravimetric and volumetric, for the determination of alpha-, beta-, and gamma-cellulose[24,24a–b] (see Chapter XII). There is increasing evidence that for many purposes solubility in other concentrations of alkali is more useful.[23a,24c–d]

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[22] O. P. Golova and V. I. Ivanov, *Bull. acad sci. U.R.S.S., Classe soc. chim.*, **1945**, 279; through *Chem. Abstracts*, **40**, 1653 (1946).

[23] W. H. Algar, H. W. Giertz, and A. M. Gustafsson, *Svensk Papperstidn.*, **54**, 335 (1951).

[23a] K. Wilson, E. Ringström, and I. Hedlund, *Svensk Papperstidn.*, **55**, 31 (1952).

[23b] B. G. Rånby, *Svensk Papperstidn.*, **55**, 115 (1952).

[23c] J. R. Simmons, *Paper-Maker (London)*, **124**, 497, 500, 502, 506 (1952).

[24] M. W. Bray, U. S. Forest Products Laboratory, Mimeographed Report **R19** (1939).

[24a] TAPPI Standard T 429 m-48 (corrected, 1948).

[24b] Analysis Committee of the Central Laboratory of the (Swedish) Cellulose Industry, *Svensk Papperstidn.*, **47**, 80, 390 (1944).

[24c] Analysis Committee of the Central Laboratory of the (Swedish) Cellulose Industry, *Svensk Papperstidn.*, **47**, 193 (1944).

[24d] R. Bartunek, *Das Papier*, **6**, 120 (1952).

B. FORMATION OF CELLULOSE

There is no generally accepted theory on the formation of cellulose. According to one hypothesis,[25–27] cellulose is formed in large plastids occurring in the cytoplasm of the living cell. At a certain stage of development these plastids burst, and the cellulose enters the cytoplasm in the form of small ellipsoidal particles 1.5 by 1.1 microns in size. These particles coalesce to form fibrils which in turn build up secondary layers on the cell wall.[4] There has been a great deal of discussion of this hypothesis, both pro and con.[28,29] Another hypothesis postulates the formation of cellulose on the cell wall. According to one form of this theory,[30] glucose undergoes its first change in the cytoplasm. Further action precipitates a substance termed "amyloid" on the cell wall which undergoes further change to "intercellose" and eventually to cellulose. With the electron microscope, Mühlethaler[31,32] has studied the formation of cellulose. In the case of bacterial cells, *Acetobacter xylinum*, a structureless capsule of slime first develops around the cell, and fibrils of cellulose are formed in this slime, presumably by polymerization of some component of the capsule. In the case of the coleoptiles of growing seed, fibrils of the primary wall form first and then those of the secondary wall. The first unit with observable structure is always a very long fibril about 300 A. in diameter. The fibrillar structure of cellulose in mature plant materials and in regenerated cellulose, its basic importance, and differing measurements of its diameter are discussed in Chapter IV. There is practically no information as to the essential chemical mechanism of the phytosynthesis of cellulose, but it is presumably enzymatic.

C. IDENTIFICATION OF CELLULOSE

The x-ray diagram is the most characteristic test for cellulose.[33,34] It requires special, expensive equipment, however, which is not universally

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[25] W. K. Farr, *Nature*, **146**, 153 (1940).

[26] W. K. Farr, *Contribs. Boyce Thompson Inst.*, **12**, 181 (1941).

[27] W. K. Farr, *J. Phys. & Colloid Chem.*, **53**, 260 (1949).

[28] D. B. Anderson and T. Kerr, *Ind. Eng. Chem.*, **30**, 48 (1938).

[29] W. K. Farr, *J. Phys. Chem.*, **42**, 1113 (1938).

[30] M. Lüdtke, *Biochem. Z.*, **233**, 1 (1931).

[31] K. Mühlethaler, *Biochim. et Biophys. Acta*, **3**, 527 (1949); discussed in R. W. G. Wyckoff, *Electron Microscopy*, Interscience, New York-London, 1949, p. 197.

[32] K. Mühlethaler, *Biochim. et Biophys. Acta*, **5**, 1 (1950).

[33] O. L. Sponsler and W. H. Dore, *Fourth Colloid Symposium Monograph*, Chemical Catalog, New York, 1926, p. 174.

[34] W. A. Sisson, *Chem. Revs.*, **26**, 187 (1940).

available. Cellulose exists in a number of crystalline modifications, which give different x-ray patterns. Cellulose I, "native cellulose," is by far the most common in nature. A second pattern can be produced by mercerization with subsequent removal of the alkali. This is called "mercerized" or "hydrate" cellulose or Cellulose II.[35] Only one case is recorded[36] where a naturally occurring cellulose gives this x-ray pattern. This is in the genus *Halicystis*. Cellulose III and IV are less well characterized and are not known to occur in nature. X-ray diagrams give evidence that cellulosic materials contain the recurring cellobiose unit but give no evidence of molecular size or distribution. Interpretation of x-ray diagrams is included in Chapter IV-B.

Acetolysis to cellobiose octaacetate also shows the presence of the cellobiose unit. This test has been of considerable use in identifying cellulose.

Another group of chemical methods includes those which indicate the presence of glucose as the only unit in the molecule. These methods are also useful, but not quite as distinctive as the preceding, since there are other polysaccharides, such as starch and glycogen, which are also made up exclusively of glucose residues. The simplest method of this type is acid hydrolysis. Another method consists of methanolysis of the fully methylated substance to be tested for glucose. If carefully carried out, this method gives other information as well. For example, the presence of methyl trimethylglucosides other than methyl 2,3,6-trimethylglucoside or of lower methyl derivatives would show the presence of polysaccharides other than cellulose; the amount of methyl tetramethylglucoside present has been used as an indication of the average molecular size.

The identification of cellulose microscopically is almost a separate problem (see Chapter IV-C). Since cellulose is anisotropic, the double refraction and the refractive indices are used as evidence, although there has been disagreement as to the correct values for the latter.[4,28,37,38] Color tests with iodine and zinc chloride, iodine and sulfuric acid, or iodine and phosphoric acid are also used.[4] It has been shown, however, that polysaccharides other than cellulose may give these tests[39] and also that poorly crystallized cellulose is stained by iodine alone,[40] as is starch. Certain dyes, such as Congo red, have also been recommended as stains, but staining reagents are not, in general, specific indicators of the presence of cellulose.[41,42]

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[35] W. A. Sisson and W. R. Saner, *J. Phys. Chem.*, **45**, 717 (1941).

[36] W. A. Sisson, *Contribs. Boyce Thompson Inst.*, **12**, 31 (1941).

[37] A. Frey, *Kolloidchem. Beihefte*, **23**, 40 (1926).

[38] A. Frey-Wyssling and K. Wuhrmann, *Helv. Chim. Acta*, **22**, 981 (1939).

[39] M. Lüdtke, *Ann.*, **456**, 201 (1927).

[40] A. Frey-Wyssling, *Verhandl. schweiz. naturforsch. Ges.*, **1939**, 67; through *Chem. Abstracts*, **35**, 6442 (1941).

Any of these tests should be combined with two very simple determinations: insolubility in hot water and solubility in cuprammonium hydroxide. The solubility characteristics set up a certain rough limit for the chain length. This is necessary as it is obvious that there must be a lower limit, admittedly ill-defined, for molecular size, below which a glucan is no longer cellulose.

That these characteristics may still be insufficient will be shown later in the discussion of animal cellulose or tunicin. Whether or not the differences in such a case as animal cellulose are real or whether they are due to contamination cannot be stated at this time.

D. SOURCES OF CELLULOSE

1. Wood Cellulose

Modern industrial requirements for vast amounts of cellulose are met by materials obtained from many different botanical sources. Woody matter, seed hairs, bast fibers, straw, stalks, hulls, and even marine plants and peat are used for various purposes. The first four constitute the important commercial sources, and the preparation of cellulose from them will be described in detail in Chapter VI. Therefore, only brief mention of these natural sources is in order here; the less important sources will be covered more fully.

Wood, the most widely used of all the cellulosic materials, is found all over the world, since it is the substance of which the branches and trunks of the higher plants are composed. There are two main classes of wood. The hardwoods or angiosperms, such as oak, are generally composed of closely packed cells with thick walls; the softwoods or gymnosperms, such as pine or cedar, are usually composed of large cells with thin walls. The composition of wood varies with the species and also with the part of the tree from which it is taken. In round numbers, on a dry basis, wood contains 40 to 50% cellulose, 20 to 30% lignin, and 10 to 30% hemicelluloses and polysaccharides other than cellulose. Resins, gums, proteins, and mineral compounds are also present. Chapter V deals with the chemistry of wood.

The utilization of wood as a material for construction, for ornament, or for fuel is outside the scope of this book, but in passing it might be stated

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[41] W. M. Harlow, N. Y. State College of Forestry, *Tech. Pub. 26*, III (1928).

[42] W. M. Harlow, *Paper Trade J.*, 112, 31 (June 5, 1941).

that practically every species is used for one or more of these purposes. The present discussion deals more directly with the fields in which cellulose is freed from noncellulosic components to produce a cellulose pulp. The pulp industry prepares the raw material for most of the viscose rayon and paper and for much of the nitrocellulose and other cellulose derivatives now being produced.

Several kinds of wood are used in the preparation of wood pulp. The most common are the pines (*Pinus* sp.), spruces (*Picea* sp.), firs (*Abies* sp.), beeches (*Fagus* sp.), poplars and aspens (*Populus* sp.), and hemlocks (*Tsuga* sp., especially *Tsuga canadensis*). There are three main chemical pulping processes. The sulfite process is used mostly on the Northern conifers, chiefly spruce, hemlock, and fir, although recently it has also been adapted for pulping young Southern pines which are free of heartwood; the sulfate (kraft) process is also used chiefly on coniferous woods, and is used widely in the southern part of the United States since it is well adapted to the Southern pines; the soda process is used on such hardwoods as aspen, gum, poplar, birch, and willow. The wood cellulose used in chemical industries (the so-called "dissolving pulps") is usually obtained by the sulfite process.[43,44] (See Chapter VI-A for detailed descriptions of these pulping processes.)

Such parts of the plant as bark, leaves, pith, knots, and trimmings may be more correctly considered as agricultural residues than as wood, but suggestions for their utilization have not been lacking, especially in the field of insulating materials and wallboard.

The magnitude of the wood cellulose industry is hard to appreciate. The United States produced 12,156,897 tons of wood pulp in 1949 and 14,810,860 tons in 1950.[45]

2. Seed Hairs

The most important of the seed hairs is cotton. Of all the commercial raw materials for cellulose, the cotton fiber contains the lowest percentage of noncellulosic material, 4 to 12%.[46] This makes purification simpler than for most cellulosic materials. In considering the cotton plant from the standpoint of cellulose, it is necessary to recognize that two types of

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[43] E. Hägglund, *Chemistry of Wood*, Academic Press, New York, 1951.

[44] L. E. Wise and E. C. Jahn, *Wood Chemistry*, 2nd ed., in two volumes, Reinhold, New York, 1952.

[45] Compiled from monthly figures, Bureau of the Census, U. S. Dept. Commerce, *Facts for Industry: Pulp, Paper and Board*, Series M14A (1951).

[46] J. D. Guthrie, C. L. Hoffpauir, M. F. Stansbury, and W. A. Reeves, U. S. Dept. Agr., Bur. Agr. Ind. Chem. *Publ. AIC-61* (revised 1949).

hair—lint and linters—are developed on the cotton seed. The differences between these and the processes for recovering and purifying the cellulose from them are discussed in Chapter VI-B.

The cotton plant belongs to the genus *Gossypium*, which has been a difficult genus to classify so that confusion exists in the enumeration and nomenclature of the species. It is probable that practically all the important commercial varieties of cotton are hybrids.[47]

Since not only the seed hairs, but also the stalks, burs, and leaves of the cotton plant are cellulosic in nature, it has been proposed that the whole plant be utilized for cellulose pulps.[48,49] Investigations of this proposal have not progressed past the experimental stage as there are still both economic and technical difficulties in the way of commercial exploitation. It has been postulated that the extracted oil might pay the total cost of production of whole cotton which would leave the residual pulp as a very cheap source of cellulose. However, the industrial value of oil extracted from the whole cotton plant has not yet been established. Experience in pulping other materials, moreover, has shown that the material should be as uniform in composition and particle size as possible, and it seems likely that the change to industrial scale will involve difficulties due to the nonuniformity of raw material. These and similar considerations will make it necessary for further experimentation to be carried out before the proposal becomes industrially attractive. The cotton stalk itself, clean and free of leaves, is technologically suited for paper pulps, but commercial production will depend largely on developing collection and storage methods.[50]

There are no other seed hairs which have found application to the same extent as cotton. Of importance is the kapok fiber, from *Ceiba pentandra*.[51] Kapok fiber is widely used as a stuffing material particularly for life preservers because of its buoyancy and resistance to moisture. It contains from 55 to 65% cellulose on a moisture-free basis, but is not used as a source of cellulose pulp. Bombax cotton obtained from several species of *Bombax* is used for wadding and upholstering. Seed hairs from certain species of *Asclepias*, such as the milkweed (*A. syriaca*), are also used in upholstery, as is the pulu fiber from fern trees of the *Cibotium* genus.[52]

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[47] H. B. Brown, *Cotton*, McGraw-Hill, New York, 1938.

[48] A. R. Macormac and F. K. Cameron, *Ind. Eng. Chem.*, **29**, 96 (1937).

[49] F. K. Cameron, *Manufacturers Record*, **110**, 30 (1941).

[50] A. J. Ernst, H. M. Sutcliffe, and S. I. Aronovsky, *Paper Ind.*, **33**, 46 (1951).

[51] S. J. Zand, *Kapok*, S. J. Zand, New York, 1941.

[52] J. M. Matthews, *Textile Fibers*, 4th ed., Wiley, New York, 1924.

3. Bast Fibers

The bast fibers are the long fibers of the inner bark of various plants. They include flax, hemp, jute, ramie, and many other less important fibers. Although widely used in textiles and paper, they have found no industrial utilization for pulps high in alpha-cellulose. The yields of the bast fibers are very small, based on the green weight of the stems. The processes used for freeing the bast fibers from the woody portion of the stem are described in Chapter VI-D.

The flax plant (*Linum usitatissimum*) is the source of the important textile fiber linen, which contains 80–90% cellulose. The fiber is most easily obtained from plants which have not fully matured, and the best linseed oil from completely ripened plants. The short fiber separated from the seed-flax straw is utilized by the paper industry. The world production of textile flax in the season 1948–49 was 496,035 tons.[53]

Many different vegetable fibers are loosely referred to as hemp. The common hemp is *Cannabis sativa*, the same plant which produces the narcotic marijuana. Bleached hemp contains approximately the same amount of cellulose as bleached linen and is similarly produced and processed. Hemp is widely used for ropes and cordage and for bagging although other fibers have replaced it to a large extent. Other bast fibers bearing the name of hemp include Sunn hemp (*Crotalaria juncea*), also called sunn, and gambo or ambari hemp (*Hibiscus cannabinus*), better known as kenaf.[54] The 1948–49 world production of true hemp was estimated at 380,294 tons.[53]

Jute is obtained from various species of *Corchorus*, especially from *Corchorus capsularis*. It has not been of much importance for the paper and pulp industry although jute waste finds some utilization. It is the cheapest of the textile fibers and is used widely for making sacks and bags. Jute fiber contains 65–75% cellulose, which is lower than the cellulose content of the preceding fibers, and around 11–12% xylan.[55,56] In 1948–49 the jute production of the world was estimated at 1,533,299 tons.[53]

Ramie, China grass, or rhea (there is some confusion as to the names)[52,57,58] is obtained from *Boehmeria nivea* (or *Urtica nivea*) and

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[53] Food and Agr. Org., United Nations, *World Fiber Review*, Bull. **14** (August 1949).

[54] R. H. Kirby, *Fibres*, **10**, 336, 365, 369, 399 (1949).

[55] A. G. Norman, *Biochem. J.*, **30**, 831 (1936).

[56] S. G. Barker, *J. Textile Inst.*, **30**, P273 (1939).

[57] G. L. Carter and P. M. Horton, *Ramie*, Louisiana State Univ. Studies **No. 26**, L.S.U. Press, Baton Rouge, 1936.

[58] B. B. Robinson, U. S. Dept. Agr., *Dept. Circ.* **585** (1940).

Boehmeria tenacissima. Its use as a textile fiber in the Orient dates back several thousand years. It has a high tensile strength and a high luster and is relatively little affected by moisture. However, its separation, purification, and processing are difficult, while its brittleness and inelasticity greatly limit its uses. Purified ramie fiber contains about 85% cellulose.[55,56] In China where cheap labor is available, very beautiful handmade fabrics are produced from this fiber. Ramie is also exported to other countries and used to a slight extent, largely in admixture with other fibers. Its use in paper has also been slight, being limited to specialty papers requiring high strength. The ramie fiber has been an important factor in elucidating the structure of cellulose, as the fibrils of which the fiber is composed are very highly oriented parallel to the fiber axis, so that a very clear x-ray diffraction pattern is obtained.

The bast fibers of the larger plants have also found some application. In the Orient the tappa or paper mulberry, *Broussonetia papyrifera*,[52] is used widely for paper and also to a certain extent in textiles. The African baobab (*Adansonia digitata*)[52] and the willow (*Salix* sp.) have been used for papermaking.[59] The bast of the castor bean plant (*Ricinus communis*) has been recommended for cordage.[60]

4. Leaf Fibers

Many of the vegetable fibers used in industry are obtained from the leaves of plants. The most important of these are the so-called hard fibers which are extensively used for cordage. Many of these are roughly and improperly classed as "hemps." In 1950 the world production of hard fibers (abacá, sisal, and henequen) was 532,410 tons.[61] For a more detailed discussion of the various leaf fibers and their processing, see Chapter VI-D.

The most important hard fiber is probably abacá or Manila hemp which is obtained from the leaf stalks of *Musa textilis*.[52] The fiber is separated mechanically from the pulp, purified, and sun-dried. To a much smaller extent other species of *Musa* have been utilized. The banana, *Musa*

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[59] M. Lüdtke, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 65 (1938).

[60] W. W. Floyd, *Southern Pulp Paper J.*, **3**, No. 2, 7 (1940).

[61] U. S. Dept. Agr., Office Foreign Agr. Relations, *Foreign Crops and Markets*, **62**, No. 21 (May 21, 1951).

sapientum,[62–66] has received a good deal of study due to its extensive cultivation and the availability of large amounts of waste.

Another important hard fiber is sisal hemp which is obtained from the leaves of *Agave sisalana.* There are many other varieties of *Agave* and related genera used for fiber, most of them coarser than true sisal. These include maguey, henequen, and cantala, all true agaves. Other hard fibers include phormium, also known as New Zealand flax or New Zealand hemp (*Phormium tenax*), and piteira or Mauritius hemp, which is obtained from *Furcraea gigantea* and other aloe plants.[52]

Another group of leaf fibers used for belts, coarse fabrics, and cordage is the bromelia fibers.[52] These are derived from various species of *Bromelia.* The best known of these is called wild pineapple and is obtained from *Bromelia pinguin.* The leaf of the true pineapple (*Ananas comosus*) also is used in textiles.[52] The fiber from the leaf of several species of yucca has been used for cordage and for paper.[59] Another important leaf fiber used for cordage and paper is caroa (*Neoglaziovia variegata*).[67]

There are a great many other leaf fibers which find limited use, some of which will be mentioned in the next subdivision.

5. Grasses, Straws, and Agricultural Residues

Since cellulose is the major constituent of the cell wall of plant life, it is clear that those plants which have no industrial utilization, as well as the residual wastes from utilized plants, form a huge potential source of cellulose. This subject is discussed more fully in Chapter VI-D. The annual production of agricultural residues in this country has been estimated at from 230 to 260 million tons on a dry basis.[68]

By far the most important of these wastes and residues, as far as their present utilization is concerned, belong to the grass family. The cereal straws in particular have long been used in the manufacture of paper and

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[62] L. Robinson-Gomez and L. L. Leonio, *Univ. Philippines Nat. and Applied Sci. Bull.*, **6**, 97 (1938); through *Chem. Abstracts*, **32**, 8774 (1938).

[63] M. J. Stacom, Brit. Patent 492,524 (Sept. 16, 1938).

[64] F. H. de Balsac, *Bull. agence gén. colonies (Paris)*, **25**, 252 (1932); through *Chem. Abstracts*, **26**, 3108 (1932).

[65] A. E. Chittenden and H. E. Coomber, *Colonial Plant and Animal Products*, **1**, 64 (1950).

[66] J. G. Kane and G. K. Maratha, *J. Indian Chem. Soc., Ind. & News Ed.*, **12**, 113 (1949).

[67] R. C. Sproull, *Paper Trade J.*, **123**, 142 (Oct. 10, 1946).

[68] *Crops in Peace and War*, U. S. Dept. Agr. Yearbook **1950–51**, Govt. Printing Office, Washington, p. 829.

paperboard.[69–71] Local production governs the type of straw used; in the United States wheat straw is most used; in the Orient, rice straw. The preparation of rayon cellulose from cereal straws has been suggested in many of the countries unable to obtain pulp.[72]

Another material extensively used for the manufacture of wallboard and insulation board is bagasse, which consists of the crushed stalks of the sugar cane (*Saccharum officinarum*) after the juice has been expressed.[69,71,73,74] Bagasse is a particularly promising material since the collection is carried out by the sugar industry and the residue is available in a clean condition at the mills. Pulp of high alpha-cellulose content has been produced from bagasse on a pilot-plant scale.[75] Similar utilization of sorgo bagasse[76,77] has been recommended. The pulping of grain sorghum residues has also been investigated, and the production of satisfactory paper and chemical pulp from several varieties has been reported.[78,79]

Cornstalks have also been widely investigated.[80] As with most stalks, problems of collection and of cleaning must be solved before any extensive utilization can take place. However, cornstalks have been used industrially in the manufacture of insulating board,[81–83] and their use for the preparation of cellulose for rayon and explosives is reported from Italy.[78]

Paper pulp has been made for some time[71,84] from esparto grass (*Stipa*

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[69] E. C. Dryden, S I. Aronovsky, and T. D. Jarrell, *Paper Ind. and Paper World*, **21**, 972 (1939)

[70] S. I. Aronovsky, *Paper Ind* , **32**, 628 (1950).

[71] E. Fischer, *Wochbl. Papierfabr.*, **78**, 432, 461 (1950).

[72] E. Goethals, *Rusta-Rayonne*, **13**, 381 (1938); through *Chem. Abstracts*, **33**, 375 (1939).

[73] E. C. Lathrop, *Ind. Eng. Chem.*, **22**, 449 (1930).

[74] C. J. West, *Scientific Report Series No. 3* (1946), Supplement to No. 3 (1949), Sugar Research Foundation, New York, N. Y.

[75] S. I. Aronovsky and D. F. J. Lynch, *Ind. Eng. Chem.*, **30**, 790 (1938).

[76] C. Levi and E. Debenedetti, *Ind carta*, **5**, 294 (1938); through *Chem. Abstracts*, **33**, 4017 (1939).

[77] E. Emiliani, *Anales soc. cient. argentina*, **51**, 8 (1951).

[78] A. Contardi and B. Ciocca, *Ricerca sci.*, **8**, **II**, 155 (1937); through *Chem. Abstracts*, **34**, 4899 (1940)

[79] E. Munds and Yung-Hui Chang, *Zellstoff-Faser*, **32**, 170 (1935); through *Chem. Abstracts*, **30**, 2752 (1936).

[80] O. R. Sweeney and L K. Arnold, *Iowa Eng. Expt. Sta. Bull.*, **No. 98** (1930).

[81] C. E. Hartford, *Ind. Eng. Chem.*, **22**, 1280 (1930).

[82] M. Krajcinovič, J. Zalesow, and F. Szücs, *Angew. Chem.*, **53**, 475 (1940).

[83] B. Wingfield, T. R. Naffziger, E. R. Whittemore, C. B. Overman, O. R. Sweeney, and S. F. Acree, U. S. Bur. Standards, *Misc. Pub.* **M123** (1936).

[84] E. Sutermeister. *Chemistry of Pulp and Papermaking*, 3d ed., Wiley, New York, 1941

tenacissima and *Lygeum spartium*) which grows in the Mediterranean region. This is also known as alfa fiber and has been recommended as a promising material for the manufacture of rayon cellulose.[72,85] Numerous other tropical grasses have also been tried out as sources of pulp, many of them with promising results.[86]

Reeds (*Arundo donax*[71,87,88] and various species of *Phragmites*) and the related cattails (*Typha* sp.)[59,88] are also receiving a great deal of attention in the search for cellulose sources. The typha fiber is reported to yield a better fiber than do the reeds.

Another plant of the grass family from which a good grade of paper pulp can be obtained is the bamboo (*Bambus, Arundinaria, Dendrocalamus,* and related genera).[71,86,89] The prediction has, in fact, been made that the woody stalks of the bamboo will form the "paper fiber of the future." [90]

In addition to stalks and straws, other products from grains and grasses have been examined. Corncobs[91,92] and rice hulls[93] are two good examples. An edible cellulose for incorporation into breakfast foods has been manufactured from rice hulls, and insulating board has been produced experimentally from corncobs.

Closely allied to the grasses is the papyrus plant (*Cyperus papyrus*)[52] which was one of the earliest raw materials for paper. In preparing the old papyri from this plant, the individual fibers were not isolated, but thin sheets of the pith were united in a manner similar to the manufacture of plywood.

A great many industrial fibers are derived from plants of the palm family. One of the more important is coir fiber, which is derived from the husks of the cocoanut (*Cocos nucifera*).[94] The husks of the betel nut (*Areca catechu*) have also been investigated with some success.[95] Others

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[85] G. Cuchiara, *Ind. carta*, **6**, 173 (1939); through *Chem. Abstracts*, **34**, 7597 (1940).

[86] J. R. Furlong and E. L. Hill, *Paper-Maker (London)*, **107**, 167 (1944); *Bull. Imp. Inst.*, **42**, 232 (1944).

[87] A. C. Rogers, *Pulp & Paper Mag. Can.*, **41**, 607 (1940).

[88] G. Jayme, K.-G. Hindenburg, and M. Harders-Steinhäuser, *Das Papier*, **2**, 45, 95 (1948).

[89] M. H. Joglekar and C. P. Donofrio, *Tappi*, **34**, 254 (1951).

[90] C. G. Schwalbe, *Proc. World Eng. Congr., Tokyo*, **1929**, **31**, 497 (1931).

[91] C. E. Hartford, U. S. Bur. Standards, *Misc. Pub.* **108** (1930).

[92] O. R. Sweeney, *Iowa Eng. Expt. Sta., Bull.*, **No. 73** (1924).

[93] E. R. Harding, *Ind. Eng. Chem.*, **20**, 310 (1928).

[94] J. Hudson, *Fibres*, **11**, 369 (1950).

[95] D. Narayanamurti, V. Ranganathan, and J. George, *Indian Forest Leaflet 112* (1947), (publ. 1948), Forest Research Institute, Dehra Dun, India.

include raffia from the leaves of *Raphia* sp. and piassava fiber from *Attalea funifera*. Piassava fibers are also obtained from other palms, such as *Raphia vinifera*.[52] The saw palmetto (*Serenoa repens*) has also been suggested as a fiber plant.[69] The cabbage palmetto (*Sabal palmetto*) has been utilized for brush fiber for some time.

The list of minor vegetable fibers is long, and it would be outside the scope of this chapter to attempt to name all of them. The cellulose content of a large number of minor fibers has been determined by Norman.[96] An idea of the variety of plants exploited may be gained by listing just a few more which might fall under the head of weeds or wastes, but which have actually been used as textile or paper fibers: nettle fiber (*Urtica dioica*),[59,88] hop fiber (*Humulus lupulus*),[59,88,97] Spanish moss (*Tillandsia usneoides*),[98] several marine plants and seaweeds[52] (*Zostera marina, Macrocystis pyrifera, Posidonia australis*), and extracted licorice root,[99] rape wastes, and thistle fiber.[88,100]

Many other products have been considered as sources of cellulosic fibers: grain and seed hulls,[69,88,101,102] soybean stems,[103] nut shells,[102,104] fruit pits,[102,105] cacti,[106] water hyacinths,[107,108] coffee beans,[109] sunflower stalks,[110] castor bean stalks,[60] and various tree, vine, or bush trimmings.[86,89,111–114] Curtailment of cellulose shipments to those countries with no good domestic source has produced an added incentive in the past few years to experiment with new sources and to repeat former experiments. From Germany, for instance, come reports of large-scale cellulose production from potato tops and stems[115,116] and of the production of cellulose satisfactory for rayon or chemical conversion from the shells of the cacao bean.[104] More critical evaluation of these reports gives a much less optimistic picture.[71,88,117–119]

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[96] A. G. Norman, *Biochem. J.*, **31**, 1575 (1937).

[97] H. M. Sutcliffe, A. J. Ernst, and S. I. Aronovsky, *The Hopper*, **6**, No 10, 4 (Jan 1950).

[98] A. Meer and L. E. Wise, *Ind. Eng. Chem., News Ed.*, **13**, 263 (1935).

[99] P. A. Houseman and H. T. Lacey, *Ind. Eng. Chem.*, **21**, 915 (1929).

[100] G. Abrahamson, *Chem. Eng. News*, **20**, 121 (1942).

[101] D. F. J. Lynch and M. J. Goss, *Ind. Eng. Chem.*, **22**, 903 (1930).

[102] G. H. Nelson, L. E. Talley, and S. I. Aronovsky, *Trans. Am. Assoc. Cereal Chemists*, **8**, 58 (1950).

[103] M. Arakawa and K. Akagi, *Rayon World (Japan)*, **5**, No. 8, 4 (1937).

[104] R. Garascia, *Gordian, Z. Gewinnung, Handel u. Verarbeit. Kakao Zucker u. verwandten Erzeug*, **46**, 17 (1940); through *Chem. Abstracts*, **34**, 5656 (1940).

[105] T. Malanos, *Z. Papier, Pappe, Zellulose Holzstoff*, **57**, 206 (1939); through *Chem. Abstracts*, **35**, 5312 (1941).

[106] F. Deplano, *Rend. seminar. facoltà sci. univ. Cagliari*, **2**, 15 (1932); through *Chem. Abstracts*, **28**, 5977 (1934).

[107] P. N. Sen-Gupta and H. K. Sen, *Science and Culture*, **3**, 442 (1938); through *Chem. Abstracts*, **32**, 3605 (1938).

[108] M. A. Azam, *Science and Culture*, **6**, 656 (1941); through *Chem. Abstracts*, **36**, 267 (1942).

[109] C. E. Nabuco de Araujo, Jr., and H. S. Polin, *Ind. Eng. Chem., News Ed.*, **19**, 877 (1941).

[110] H. Rauch, *Angew. Chem.*, **53**, 568 (1940).

6. Cellulose outside the Vegetable Kingdom

Cellulose is not confined to the vegetable kingdom. It is also found in the mineral and animal kingdoms. In the former, to be sure, it occurs in products of vegetable origin, being found in fossil woods,[120] peat,[121] and certain types of lignite.[122] There is practically none in bituminous coal. Peat and lignite fiber have found some utilization in paperboard,[123] in insulating sheets,[124,125] and even in textiles.[52] There is also a "mineral cellulose," sapperite,[125,126] which is produced from fossil vegetable matter and is found associated with lignite. It consists of white to light-brown fibers soluble in cuprammonium solution. It burns, leaving a light ash,

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[111] T. L. Crossley, *Pulp & Paper Mag. Can.*, **39**, 568 (1938); through *Chem. Abstracts*, **32**, 8137 (1938).

[112] L. G. S. Hebbs and E. L. Hill, *Paper-Maker (London)*, **112**, TS28 (1946).

[113] A. J. Ernst, H. M. Sutcliffe, and S. I. Aronovsky, *Tappi*, **34**, 247 (1951).

[114] H. M. McKenzie, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **27**, TS375 (1946).

[115] P. Reinhold, *Vierjahresplan*, **4**, 699 (1940); through *Chem. Abstracts*, **35**, 2717 (1941).

[116] M. Lüdtke, *Cellulosechemie*, **18**, 5 (1940).

[117] K. Ward, Jr., *FIAT Final Rept.* 439, Joint Intelligence Objectives Agency.

[118] G. Jayme, *FIAT Rev. of German Science* 1939–1946, *Preparative Org. Chem.*, Part III, p. 49.

[119] H. Hammer, *Wochbl. Papierfabr.*, **77**, 168 (1949).

[120] W. A. Gortner, *J. Am. Chem. Soc.*, **60**, 2509 (1938).

[121] R. Potonié and W. Benade, *Braunkohle*, **28**, 335 (1929); through *Chem. Abstracts*, **23**, 4552 (1929).

[122] E. Opfermann and G. Rutz, *Papier-Fabr.*, **28**, Tech.-wiss. Tl., 780 (1930).

[123] R. Beyschlag, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 105 (1938).

[124] A. Patla, *Przeglad Górnicza-Hutniczy*, **31**, 352 (1939); through *Chem. Abstracts*, **35**, 4937 (1941).

[125] K. Overlack, *Wochbl. Papierfabr.*, **72**, 33 (1941); through *Chem. Abstracts*, **35**, 4593 (1941).

[126] W. Gothan, *Braunkohle*, **21**, 400 (1922); through *Chem. Abstracts*, **18**, 211 (1924).

and gives a blue coloration with the zinc chloride–iodine reagent.[127] The existence of cellulose in these materials is evidence of its great stability under the proper conditions. There is no record of cellulose being found in connection with any of the great petroleum deposits, which may be of animal origin rather than vegetable. However, cellulose has been reported in sapropel,[128] which has been suggested as an intermediate stage in the formation of petroleum.

Cellulose has also been reported in the animal kingdom. At least a material is found which gives the same x-ray pattern as cellulose[129] and can be acetolyzed or hydrolyzed to the same products.[130] It differs from cellulose in yielding different volumes of gas on destructive distillation[131] and in certain aspects of its viscosity relations.[131a] This material, called tunicin or animal cellulose, is obtained from the outer mantles of certain marine organisms belonging to the class of the *Tunicata*, such as *Phallusia mamillata, Polycarpa varians*, and *Ascidia mentula*.[132] Recent investigations on this material[133,134] suggest that tunicin is identical chemically with cellulose, but that its degree of lateral order may be even higher, as indicated by a sharper x-ray diagram. There is, however, some evidence indicating a slight difference in chemical structure, possibly a certain degree of branching of the polymeric chain.[131a]

7. Lichenin

Although the differences between lichenin and cellulose are now definitely established, the former was considered as a type of cellulose for so long that it should be mentioned in any discussion of the natural occurrence of that material. Lichenin, an important constituent of the cell wall of Iceland moss (*Cetraria islandica*), has many of the characteristics of cellulose. It can be quantitatively hydrolyzed to glucose[135] and can be converted to cellobiose either enzymatically[136] or by acetolysis.[137] On the other hand it is soluble in hot water. Moreover, the x-ray diagram[138] and the optical rotation of its derivatives do not agree with those of cellulose. The structure of lichenin seems to have been established by Meyer and Gürtler[139] and confirmed by Boissonnas.[140] On the basis of oxidation with periodic acid and of investigation of the hydrolysis of methyl lichenin, it has been established that only about 70% of the linkages in lichenin are 1,4 as in cellulose, the remainder being 1,3.

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[127] H. Meixner, *Zentr. Mineral., Geol.*, **1938A**, 208; through *Chem. Abstracts*, **32**, 6983 (1938).

[128] E. I. Kazakov and B. A. Tovbin, *Trudy Lab. Genesiza Sapropelya*, **1939**, No. 1, 165; through *Chem. Abstracts*, **34**, 5710 (1940).

[129] R. O. Herzog and H. W. Gonell, *Z. physiol. Chem.*, **141**, 63 (1924).

[130] L. Zechmeister and G. Tóth, *Z. physiol. Chem.*, **215**, 267 (1933).

[131] G. Viel, *Compt. rend.*, **208**, 1689 (1939).

[131a] A. J. A. van der Wyk and J. Schmorak, *Helv. Chim. Acta*, **36**, 385 (1953).

[132] R Sutra, *Compt. rend.*, **195**, 181 (1932).

[133] K. H. Meyer, L. Huber, and E. Kellenberger, *Experientia*, **7**, 216 (1951)

[134] B. G. Rånby, *Arkiv för Kemi*, **4**, 241 (1952).

[135] M. Hönig and S. Schubert, *Monatsh.*, **8**, 452 (1887)

E. NATURAL OCCURRENCE OF COMBINED CELLULOSE

Whether or not there is any natural occurrence of chemical compounds of cellulose is still a moot point. Combination of cellulose with xylan or with lignin are two possibilities which have been extensively studied. The status of these two possibilities will be discussed in Sections B and C, respectively, of Chapter V. Of the compound celluloses postulated by early workers (lignocellulose, pectocellulose, cutocellulose), lignocellulose is the only one for which there is good evidence for its existence, yet even here the evidence is conflicting.

Cork was believed for some time to contain esters of cellulose with the higher fatty acids.[141] More recent work[142–144] has tended to show that the acids in cork are not combined chemically with the cellulose, as these esters have been synthesized and do not have the properties of cork.

In the possibilities just discussed, there is no marked difference in physical properties to indicate a chemical rather than a physical combination. A somewhat different case is met with in certain plant mucilages, which are water-soluble, but on hydrolysis yield an insoluble residue which has been considered as cellulose. There is reason to consider some of these materials as substances related to cellulose rather than as true cellulose, but the relation in some cases must be very close indeed.

Quince-seed mucilage (*Cydonia vulgaris*) is a good example. The mucilage can be extracted with cold water and is apparently a neutral salt, the free acid of which is insoluble in water, as it can be precipitated by acidification and will redissolve only if the mixture is made slightly alkaline. Hydrolysis with 0.5 N H_2SO_4 gives 33% insoluble residue.[145] Part of this is soluble in 17.5% NaOH, but there is an insoluble residue of about 24% (based on the original mucilage). Hydrolysis by the Monier-Williams method gives 78% of crystalline glucose (cotton by the same method yields about 91%).[146] Other positive tests for cellulose given by this residue are a blue color with the sulfuric acid and iodine reagent and solubility in cuprammonium hydroxide.

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[136] H. Pringsheim and W. Kusenack, *Z. physiol. Chem.*, **137**, 265 (1924).

[137] P. Karrer, B. Joos, and M. Staub, *Helv. Chim. Acta*, **6**, 800 (1923).

[138] R. O. Herzog, *Z. physiol. Chem.*, **152**, 119 (1926).

[139] K. H. Meyer and P. Gürtler, *Helv. Chim. Acta*, **30**, 751 (1947).

[140] R. A. Boissonnas, *Helv. Chim. Acta*, **30**, 1703 (1947).

[141] A. Grün and F. Wittka, *Z. angew. Chem.*, **34**, 645 (1921).

[142] P. Karrer, J. Peyer, and Z. Zega, *Helv. Chim. Acta*, **5**, 853 (1923).

[143] F. Zetsche and G. Rosenthal, *Helv. Chim. Acta*, **10**, 346 (1927).

[144] A. Madinaveitia and T. Catalán, *Bol. acad. cienc. (Madrid)*, **1**, No. 2, 9 (1935); through *Chem. Abstracts*, **30**, 3022 (1936).

The mucilage from cress-seed (*Lepidium sativum*) yields 18% of insoluble residue similarly to quince-seed mucilage.[147] Hydrolysis by the Monier-Williams method gives 90% of the theoretical yield of glucose, determined by the hypoiodite method. This cellulosic residue contains 1.8% of uronic anhydride. This may arise from an impurity or from the main constituent, if, for example, the cellulose has been partially oxidized.

White mustard seed (*Brassica hirta*) contains a mucilage similar to the preceding. The residue from hydrolysis with dilute sulfuric acid or dilute alkali consists of about 50% of the original mucilage and has the following characteristics of cellulose. It is soluble in concentrated zinc chloride solutions, gives a blue color with zinc chloride and iodine, is acetylated to a triacetate, and can be hydrolyzed by the Monier-Williams method to 72.5% of the theoretical yield of glucose, estimated from the reducing power on Fehling solution. This residue contains 3.4% uronic anhydride groups.[148]

Other mucilages, for instance, slippery-elm bark mucilage,[149] give similar insoluble residues on hydrolysis, usually in smaller amounts. A more complete identification of the residue as cellulose might be desirable, as, for instance, by the x-ray pattern, but the identification is sufficiently satisfactory to make it clear that the substance must at least be closely related to cellulose. The solubility of the mucilages in water is probably due to the presence of the neutral salt groups.

The aim of this chapter has been to indicate the extent to which cellulose exists in nature and to point out some of the more interesting sources of this important material. Many of the points touched on will be treated more fully in the later portions of this book.

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[145] A. G. Renfrew and L. H. Cretcher, *J. Biol. Chem.*, **97**, 503 (1932).

[146] G. W. Monier-Williams, *J. Chem. Soc.*, **119**, 803 (1921).

[147] K. Bailey, *Biochem. J.*, **29**, 2477 (1935).

[148] K. Bailey and F. W. Norris, *Biochem. J.*, **26**, 1609 (1932).

[149] E. Anderson, *J. Biol. Chem.*, **104**, 163 (1934).

Chapter III

CHEMICAL NATURE OF CELLULOSE AND ITS DERIVATIVES

A. HISTORICAL SURVEY[1,2]

CLIFFORD B. PURVES

1. The Concept of Cellulose

Although cotton and linen had been prepared and used from earliest times, the history of the chemistry of cellulose really began in the period 1837–1842 with the investigations of the French agriculturist Anselme Payen. Phillips,[3] and Reid and Dryden,[4] published accounts of Payen's life and researches. Payen studied starch extensively and obtained the enzyme diastase in a crude condition. He clearly recognized that starch was a reserve carbohydrate in plants and formed the opinion that another polysaccharide must be present in the permanent structure of the cell wall. At that time it was customary to extract plant tissue with very mild reagents, such as alcohol and water, and to submit the dried residue to elementary analysis on the assumption that it was a uniform chemical individual. Since the analyses varied from plant to plant, the general impression was that the cell wall consisted of a uniform, woody or ligneous substance peculiar to each species and that it probably contained rather more carbon and hydrogen than a carbohydrate should. Payen rejected the published carbon contents of 47 to 51% for "pure" plant tissues, not because the analyses were faulty, as some thought, but because the plant skeleton must have been insufficiently purified from the woody and fatty materials with which it became incrusted during growth.

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[1] The first portion of this survey was guided to a considerable extent by that of K. Hess, *Die Chemie der Zellulose,* Akadem. Verlagsgesellschaft, Leipzig, 1928, pp. 24–36. This work contains many additional references.

[2] See also J. König and E. Rump, *Chemie und Struktur der Pflanzen-Zellmembran,* J. Springer, Berlin, 1914, pp. 5–43, which has many references.

[3] M. Phillips, *J. Wash. Acad. Sci.,* **30,** 65 (1940).

[4] J. D. Reid and E. C. Dryden, *Textile Colorist,* **62,** 43 (1940).

In order to mitigate this difficulty during purification, Payen[5] first examined very young plant formations such as seeds, cotton lint, rootlets from herbaceous and woody species, pith from young elder shoots, cucumber tissue, and various leaves as well as a few mosses and lichens. The newly gathered materials were alternately extracted with dilute hydrochloric acid and dilute ammonia, then with water, alcohol, and ether. In every case, the residues contained 43.6 to 45.0% of carbon, 6.0 to 6.5% of hydrogen, and the remainder was oxygen. The residues gave dextrorotatory, gummy materials (dextrins) and eventually a dextrorotatory reducing sugar (dextrose) when boiled with dilute acid,[6] although not when submitted to the action of diastase. These observations convinced Payen that the fibrous warp and woof of all young plant cells consisted of one uniform chemical individual which was a carbohydrate based on glucose residues and isomeric with starch (C, 44.4%; H, 6.2%). As starch gave a blue color with iodine immediately, while the new carbohydrate had first to be somewhat swollen with sulfuric acid, the latter polysaccharide was regarded as the more compact or more highly "aggregated" isomer. Payen named it cellulose.[5]

More drastic methods were necessary to isolate cellulose from mature hardwood (oak). These included the use of nitric acid at 36°C., and the suspension of the finely divided material in boiling caustic soda followed by evaporation almost to dryness. Still more difficulties were encountered with a mature coniferous wood (fir) and resort was made to a chlorination, although Payen noted that aqueous chlorine was not without an effect on the cellulose and had to be used with circumspection.

If cellulose was the fundamental, uniform constituent of all plant cell walls, the variation in the over-all composition of plant tissue was caused by variation in the composition of the materials entrapped in the cell wall with the cellulose. In order to check this point, several very finely divided woods were extracted with water, alcohol, weak aqueous acid, and weak alkali.[7] After this preliminary purification, the samples were evaporated with four to five times their weight of strong alkali so that the final temperature was between 150° and 200°C. Two or three extractions left the cellulose pure, and the alkaline extracts on acidification gave fawn-colored precipitates containing 53.7 to 59.4% of carbon depending on their origin. The precipitate from beech was eventually divided into four fractions with the properties shown in Table 1.

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[5] A. Payen, *Troisième Mémoire sur les Développements des Végétaux*, Extrait des Mémoires de l'Académie Royale des Sciences. Tome VIII des savants étrangers, Imprimérie Royale, Paris, 1842.

[6] H. Braconnot, *Ann. chim. phys.*, **12**, 172 (1819).

[7] A. Payen, *Quatrième Mémoire sur les Développements des Végétaux*, Extrait des Mémoires de l'Académie Royale des Sciences. Tome VIII des savants étrangers, Imprimérie Royale, Paris, 1842.

TABLE 1

Noncellulose Fractions from Beechwood (Payen[7])

Fraction	Per cent C	Per cent H	Solubility
1	46.1	6.1	Insoluble in alcohol, ether, ammonia
2	50.1	5.8	Insoluble in alcohol, ether; soluble in ammonia
3	62.3	5.9	Insoluble in ether; soluble in alcohol, ammonia
4	67.9	6.9	Soluble in alcohol, ether, ammonia; slightly soluble in water

Payen recognized that the noncellulose part of wood tissue consisted of several components which varied in their relative amount, and perhaps in their chemical nature, from species to species. Although direct evidence concerning the relationship of these substances to each other in the plant was lacking, Payen expressed the opinion that two or three of them were of an acidic nature and might originally have been combined as acids are combined in fats.

Some botanists soon disputed the uniformity of cellulose[8] and based their opposition on the fact that preparations from different plants varied widely in staining reactions and solubility in cuprammonium. Fremy,[9] who clearly understood the enzymatic conversion of insoluble to soluble pectin forms during the ripening of fruit, was prominent in maintaining that the cell wall was composed of several substances. These substances included "meta," "para," and other celluloses which differed among themselves in solubility. Pelouze[10] showed that cellulose regenerated from cuprammonium solution was soluble in weaker acid than the very concentrated hydrochloric acid required to dissolve the original material readily. Immediate dilution of the latter solution precipitated cellulose, but dilution after one or two days' standing did not do so. Cellulose, when heated in caustic potash at 150° to 190°C., became soluble in cold alkali without losing its capacity to yield reducing sugars on acid hydrolysis. Payen admitted that chemical treatments might modify the physical properties of cellulose by modifying its "state of aggregation." He nevertheless maintained, in opposition to Fremy and others, that naturally occurring specimens were uniform when properly isolated.

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[8] *Jahresber. der Chem.*, **12**, 529–41 (1859), reviews these discussions in detail.

[9] E. Fremy, *Jahresber. der Chem.*, **1**, 796 (1847–48).

[10] T. J. Pelouze, *Compt. rend.*, **48**, 327 (1859); *J. pharm., chim.*, [3], **35**, 88, 209 (1859).

Payen's opinion that cellulose was constituted invariably of glucose residues was based of necessity on inadequate data, because really reliable methods of discriminating one monosaccharide from another were not available until the decade 1880–1890. Acid hydrolyzates of many celluloses were then found to contain substantial amounts of galactose, arabinose, mannose, or xylose, as well as glucose. The endosperm of the ivory nut, for example, which Payen had thought an especially pure cellulose, yielded mannose almost exclusively,[11] while the cellulose of Iceland moss was eventually recognized as lichenin. Schulze,[12] who reviewed the literature, noted that most of the polysaccharides which yielded these other sugars were much more readily hydrolyzed than the remaining cellulose by aqueous acid and were extracted from the cell wall by aqueous alkali (cf. Payen's incrusting Fraction 1, Table 1). Schulze reserved the term cellulose for the constituent more resistant toward aqueous acid and freely soluble in cuprammonium. The less-resistant carbohydrates, derived for the most part from sugars other than glucose, were given the generic name of hemicelluloses. The differentiation, however, was not clean-cut because quite drastic extractions with acid and alkali failed to remove all of the hemicelluloses. Xylans and mannans, in particular, were partly but tenaciously retained by the cellulose residue. This circumstance prevented Schulze from claiming that cellulose invariably resembled cotton cellulose in containing nothing but glucose residues; indeed, three out of eleven different specimens gave hydrolyzates containing other sugars.

The noncellulose part of alcohol-ether-extracted plant tissue, called incrusting or ligneous matter by Payen, included, therefore, hemicelluloses as well as pectins.[9,13] As the latter groups of substances were gradually recognized as distinct entities, the term lignin (Fremy's "vasculose"[14]) became restricted to denoting the noncarbohydrate fraction of the noncellulose incrustants[15,16] (cf. Payen's Fractions 3 and 4, Table 1). This clarification in ideas and in nomenclature did much to explain the variation in staining reactions and general behavior that had led Fremy and others to deny the chemical uniformity of cellulose. Payen's argument assumed that the cellulose was isolated in a chemically unchanged form and the assumption was repeatedly supported by demonstrations that the cellulose[5,12,14,17] and the lignin[12,17] could be separately isolated as porous masses that retained the shape and detailed microscopic aspect of the original tissue. The latter was accordingly heterogeneous on the microscopic scale and it consequently could not be homogeneous on the molecular scale, as a uniform chemical combination between cellulose and incrusting substances demanded.

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[11] R. Reiss, *Ber.*, **22**, 609 (1889).

[12] E. Schulze, *Ber.*, **24**, 2277 (1891); *Z. physiol. Chem.*, **16**, 387 (1892).

[13] B. Tollens, *Ann.*, **286**, 292 (1895).

[14] E. Fremy, *Compt. rend.*, **48**, 275 (1859); *J. pharm. chim.*, [3], **36**, 5 (1859).

[15] F. Schulze, *Jahresber. der Chem.*, **10**, 491 (1857); *Chem. Zentr.*, **1857**, 321.

[16] G. Dragendorff, *Die qualitative und quantitative Analyse von Pflanzen und Pflanzenteilen*, Vandenhöck und Ruprecht's Verlag, Göttingen, 1882, pp. 256–61. English translation by H. G. Greenish, Baillière, Tindall, and Cox, London, 1884, pp. 252–57.

It was extremely unfortunate that many chemists failed to appreciate the force of the microscopic evidence and became unduly impressed with the regularities to be observed in the macroanalysis of cell-wall material. It had to be admitted that the isolation of cellulose frequently required the use of drastic chemical reagents, such as the nitric acid–potassium chlorate mixture introduced by Schulze,[15] and that cellulose itself was not always left unchanged by these reagents. With this background, it was plausible to argue that cellulose was an artifact produced by chemical change during isolation and to accept the varying physical properties of incrusted material, such as insolubility in cuprammonium, as evidence that the original tissue was a homogeneous chemical complex probably peculiar to each species of plant. Although earlier botanists, including Fremy, occasionally seemed to subscribe to this outlook, it first found full expression in the publications of Erdmann,[18] who considered the woody concretions sometimes found in pears to be "glycodrupose," $C_{24}H_{36}O_{16}$, while spruce wood was "glycolignose," $C_{30}H_{46}O_{21}$. Mild acid hydrolysis left "drupose," $C_{12}H_{20}O_8$, and "lignose," $C_{18}H_{26}O_{11}$, respectively, by the loss of reducing sugar. Subsequent extractions with dilute nitric acid progressively oxidized away an aromatic group related to catechol to leave a nearly constant over-all yield of wood fiber. Although Erdmann's views did not pass uncriticized,[19] they later received support from many quarters and particularly from Cross and Bevan.[20] These authors claimed that jute and other bast fibers were uniform in elementary composition, chemical reactions, staining behavior, and

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[17] J. König and E. Rump, *Chemie und Struktur der Pflanzen-Zellmembran*, J. Springer, Berlin, 1914, pp. 85–88, plates 1–7.

[18] J. Erdmann, *Ann.*, **5**, supplementary binding, 223 (1867).

[19] R. Sachsse, *Die Chemie und Physiologie der Farbstoffe, Kohlenhydrate und Proteinsubstanzen*, L. Voss, Leipzig, 1887, pp. 150–52.

[20] C. F. Cross and E. J. Bevan, *J. Chem. Soc.*, **38**, 666 (1880); **41**, 90 (1882); **43**, 18 (1883); **55**, 199 (1889); *Cellulose*, 1st ed., 1895; 2d ed., 1903; 3d ed., 1916; *Researches on Cellulose, 1895–1900; 1900–1905; 1905–1910*, Longmans, Green & Co., London.

microscopic appearance along their length. The residue obtained after partial solution gave the same analytical figures, and the fibrous structure was retained during oxidation, chlorination, acid hydrolysis, and treatments with aqueous sodium sulfite. On this basis, jute was "bastose," or $C_{76}H_{80}O_{37}$,[21] while related names and formulas were given to derived products. Cross and Bevan believed that in the plant the cellulose, pectin, lignin, and fatty material merged into one another by insensible chemical gradations and they called the original complexes "ligno-," "pecto- or muco-," "adipo- or cuto-cellulose" according to the constituents preponderating in a given fiber. "Cellulose" was merely the aggregate resulting from a chemical breakdown carried to the point where the reactions generally accepted for pure cellulose were obtained. This view, indefatigably upheld and amplified,[20,22] had many adherents during the period 1880 to 1920.

Although the lignocellulose theory was never much more than a reversion to a pre-Payen outlook, its protagonists were obviously not to be convinced of its inadequacy by any evidence that involved the use of chemicals. Rebuttal came through physical studies on the birefringence and swelling of cellulose fibers by Nägeli, Ambronn, and their successors and by the development of x-ray technique (Chapter IV). These studies gradually built up an overwhelming case for the modern concept of fibrous cellulose as being an essentially crystalline body, shot through and through with submicroscopic faults and disorganized localities. It was incredible that a uniform, regularly organized crystal lattice could be in uniform chemical combination throughout its bulk with large, amorphous molecules of lignin, fat, or hemicellulose substances. The gradual abandonment of the lignocellulose theory may be dated from 1920, when Herzog and Jancke[23] showed that lignified fibers, jute and lime (linden) wood, gave practically the same x-ray pattern as delignified wood pulp or as flax, ramie, or cotton. Microdissections of woods[24] and x-ray studies on the submicroscopic porous structure of cellulose[25] now showed beyond doubt that the incrustants tend to be concentrated in the capillaries and between individual cells.

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[21] C. F. Cross and E. J. Bevan, *J. Chem. Soc.*, **55**, 199 (1889).

[22] C. F. Cross and C. Dorée, *Researches on Cellulose, 1910–1921*, Longmans, Green & Co., London, 1922. A discussion opened by H. Wenzl describes a revival of rather similar views in the 1940's by F. Schütz, and, to some extent, by R. S. Hilpert, together with detailed rebuttals by A. Frey-Wyssling, K. Hess, and G. Jayme, *Holzforschung*, **2**, 33, 65 (1948). See also L. E. Wise, *Pulp & Paper Mag. Can.*, **50**, Convention Issue, 179 (1949).

[23] R. O. Herzog and W. Jancke, *Ber.*, **53B**, 2162 (1920).

[24] A. J. Bailey, *Ind. Eng. Chem., Anal. Ed.*, **8**, 52, 389 (1936).

[25] A. Frey-Wyssling, *Protoplasma*, **25**, 261 (1936). This article contains an excellent discussion of the earlier literature.

This modern conclusion is entirely in line with a theory of incrustation enunciated by Wislicenus[26] in 1910. The early spring sap of various trees was treated with filter paper or alumina gel and only 4 to 8% of the total solids was adsorbed from solution. The adsorbed material was assumed to represent the colloidal, as opposed to the crystalloidal, contents of the sap. Cambial sap, isolated at the height of the growing season, contained up to 37% of colloids, but when growth stopped in the late summer the amount fell sharply to 6 to 8%. Incrustation was therefore regarded as a physical process in which the sap colloids coagulated or were adsorbed upon the enormous internal surface of a previously elaborated, highly porous cellulose framework. The question as to whether or not a few main valence bonds establish themselves between the cellulose surface and the adsorbed incrustants is discussed in Chapter V.

Although the general acceptance of the micellar theory now renders the concept of lignocellulose, together with the associated nomenclature, quite obsolete, the historical controversies about a proper definition of cellulose have not yet been entirely resolved. The fibrous, delignified pulps isolated by one procedure or another, as by the alternating chlorination–sodium sulfite extractions of Cross and Bevan,[27] are still often named celluloses, especially in textile and botanical circles. On this basis, cellulose is the natural, fibrous, carbohydrate, structural aggregate of the cell wall[28,29] and usually includes a hemicellulose fraction yielding sugars other than glucose on acid hydrolysis. Cotton cellulose, consisting entirely of glucose residues, is thus an abnormal type.[28] The alternative definition follows Payen and Schulze in accepting cotton as a standard and consequently restricts the term cellulose to that portion of the cell wall derived exclusively from glucose and resembling cotton cellulose in its physical and chemical properties. This definition has been openly or tacitly adopted by the great majority of those interested mainly in studies of chemical structure, which almost invariably have been carried out with cotton or filter paper.

While it is true that the deeper insight of today enables a careful author to oscillate between the two definitions and yet remain intelligible, the double standard created great confusion in the past. In the interest of clarity as well as in deference to the brilliant pioneering of Payen, it seems desirable to use the unmodified term cellulose in Payen's sense and to denote as pulps all aggregates known to contain hemicellulose fractions. Particular aggregates, of course, may also be very properly described by qualifying the word cellulose, as, for example, alpha-cellulose, or Cross and Bevan cellulose.

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[26] H. Wislicenus, *Kolloid-Z.*, **6**, 87 (1910); **27**, 209 (1920).

[27] C. F. Cross and E. J. Bevan, *J. Chem. Soc.*, **38**, 667 (1880).

[28] A. G. Norman, *The Biochemistry of Cellulose, the Polyuronides, Lignin, etc.*, Clarendon Press, Oxford, 1937, pp. 1–4.

[29] J. T. Marsh and F. C. Wood, *An Introduction to the Chemistry of Cellulose*, Chapman & Hall, London, 1938; D. Van Nostrand Co., New York, 1939, p. 1.

2. Discoveries of Industrial and Theoretical Interest

In addition to the rather botanical lines of research just described, the nineteenth century witnessed several disconnected developments which became of great technical importance. Payen's use of strong hot alkali and of chlorine for pulping woods and grasses led, in the 1860's, to the establishment of the kraft and sulfate industries[30] while the sulfite process was first described by Tilghman,[31] of Philadelphia. Schwalbe's textbook[32] gives a more detailed, tabular review of progress in this field.

The self-taught English chemist Mercer made many contributions to the technique of dyeing and printing calico in the period 1840 to 1860 but his discoveries were not generally known until a later date.[33,34] About 1844, he carefully studied the action of cold, strong caustic soda on cotton yarn and noted the shrinkage in dimensions, and the increase in strength, in affinity for dyes, and in the weight of the washed and air-dried product[35] (mercerized yarn). The process was interpreted as involving an intermediate alkali cellulose complex $(C_6H_{10}O_5)_2.Na_2O$, and as giving a cellulose hydrate $(C_6H_{10}O_5)_2 . H_2O$. Mercer's patent on this process (1850) also included the parchmentizing effect of strong sulfuric acid[36,37] and zinc chloride solutions on paper and yarn. Mercer, in addition, gave a detailed description of the solubility of cotton in strong cuprammonium solution,[38] and of the regeneration of the cellulose on the addition of acid. These observations led in time to the large-scale production of cellulose xanthates (viscose) and benzoates.[39] Leuchs,[40] Lilienfeld,[41] and Denham and Woodhouse[42] independently but almost simultaneously used alkali cellulose and an alkyl halide[43] or sulfate to prepare the alkylated derivatives. The cuprammonium rayon industry, however, probably originated with the independent duplication of Mercer's observations by Schweizer[44] and their amplification by Cramer[45] and Schlossberger.[46]

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[30] A. Mellier, patented in France in 1854 and applied to woods about 1865. Quoted from Hess, *Die Chemie der Zellulose*, Akadem. Verlagsgesellschaft, Leipzig, 1928, p. 244.

[31] B. C. Tilghman, abstracts in *Bull. soc. chim.*, [2], **8**, 137 (1867); *Ann. génie civil*, p. 271 (Apr., 1867); *Jahresber. der Chem.*, **20**, 952 (1867). See also A. Mitscherlich, *Jahresber. der Chem.*, **1876**, 1172; *Dinglers Polytech. J.*, **220**, 479, 564 (1876); and W. B. Wheelwright, *Paper Makers J.* (U. S.), **39**, 20 (1940).

[32] C. G. Schwalbe, *Die Chemie der Cellulose*, Gebrüder Bornträger, Berlin, 1911, p. 509.

[33] Obituary in *J. Chem. Soc.*, **20**, 395 (1867).

[34] E. A. Parnell, *The Life and Labours of John Mercer*, Longmans, Green & Co., London, 1886, pp. 175–207, 214–16, 317.

[35] The question of priority is discussed by the editors of *The Dyer and Calico Printer* in *Mercerization. A Practical and Historical Manual*, Vol. I, Heywood and Co., London, 1903, pp. 1–10. A. Wurtz, *Dictionnaire de Chemie*, Vol. I, Hachette and Co., Paris, 1876, p. 779, attributes the discovery of mercerization to Persoz. Girard, *Ann. chim. phys.*, [5], **24**, 337 (1881), states that the initial publication was by Persoz in 1846. See also Schwalbe, *Die Chemie der Cellulose*, Gebrüder Bornträger, Berlin, 1911, p. 37.

In 1833, Braconnot,[47] following up an observation of Pelouze, showed that pure, anhydrous nitric acid differed from the dilute acid in having little effect on insoluble alkali and alkaline earth carbonates. Braconnot was led to try the action of the anhydrous acid on various polysaccharides, including cotton, linen, and wood shavings. The highly flammable, neutral powders (xyloidins) dissolved in concentrated acetic acid and the solutions deposited tough, varnish-like films as clear as glass. The somewhat more highly nitrated guncottons were independently discovered by Böttger[48] and by Schönbein,[49] who obtained products of technical value by

[36] J. A. Poumarède and L. Figuier, *J. pharm chim.*, **11,** 81 (1847); *J. prakt. Chem.*, **42,** 25 (1847).

[37] C. E. Guignet, *Compt. rend.*, **108,** 1258 (1889). This type of parchmentized cellulose was frequently called "Guignet cellulose."

[38] Quoted from C. F. Cross and E. J. Bevan, *Cellulose*, 1st ed., Longmans, Green & Co., London, 1895, p. 13.

[39] C. F. Cross, E. J. Bevan, and C. Beadle, *Ber.*, **26,** 1090 (1893).

[40] O. Leuchs, German Patent 322,586 (Jan. 26, 1912). Quoted from Hess, *Die Chemie der Zellulose*, Akadem. Verlagsgesellschaft, Leipzig, 1928, p. 429.

[41] L. Lilienfeld, Brit. Patent 12,854 (May 31, 1912); through *Chem. Abstracts*, **7,** 3839 (1913).

[42] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **103,** 1735 (1913).

[43] M. Berthelot, *Ann. chim. phys.*, [3], **60,** 103 (1860), probably obtained a crude, partly alkylated sucrose by heating the sugar with a mixture of potassium hydroxide and ethyl bromide.

[44] E. Schweizer, *J. prakt. Chem.*, **72,** 109 (1857).

[45] C. Cramer, *J. prakt. Chem.*, **73,** 1 (1858).

[46] J. E. Schlossberger, *J. prakt. Chem.*, **73,** 371 (1858).

[47] H. Braconnot, *Ann.*, **7,** 242, 245 (1833). An addendum by J. Liebig notes that Braconnot's products contained nitrogen and detonated weakly on heating.

[48] C. F. Schönbein and R. Böttger, *Poggendorff's Ann. der Physik und Chemie*, **70,** 320 (1847).

[49] C. F. Schönbein, *Phil. Mag.*, **31,** 7 (1847).

using concentrated sulfuric acid as a catalyst in the nitration. It is interesting to note that by 1847 the most highly nitrated cellulose nitrate was correctly recognized as one in which three molecules of water per glucose residue had been replaced by the elements of three molecules of nitric acid,[50,51] and that the partial denitration of guncotton to pyroxylin in dilute nitric acid led Gladstone[52] to suggest that the nitration reaction was an equilibrium. Schützenberger,[53] who acetylated cellulose with hot acetic anhydride, was also prompt to recognize that the most highly substituted acetate was a triacetate. He was not interested in the analyses of lower acetates owing to the probability that they were mixtures containing unchanged cellulose. The use of concentrated sulfuric acid or zinc chloride as a catalyst in the acetylation was introduced by Franchimont,[54] who noted that the progressive increase in the crystallinity of the products obtained with various conditions paralleled the decrease in molecular complexity toward that of acetylated glucose. This research unearthed the crystalline octaacetate of the reducing disaccharide cellobiose,[55] although an analytical error caused Franchimont to consider it as a fully acetylated trisaccharide. Cross and Bevan[56] studied the preparation of cellulose triacetate, and a method of partial deacetylation introduced by Miles[57] opened the way to modern, acetone-soluble derivatives.

The cause of the "tendering" of fabrics during bleaching with hypochlorite and during other textile operations remained an enigma until the period 1880–1883, when Girard and especially Witz published researches on the subject which still merit detailed study. Girard[58] showed that acids of any sort, organic, inorganic, strong or weak, in dilute or concentrated aqueous solution, in the gaseous state or dried into the cloth, invariably reduced the tensile strength to zero and yielded a water-insoluble friable

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[50] Some contemporaneous analyses were discordant. See reviews in *Ann.*, **64**, 391 (1847) and *Jahresber. der Chem.*, **1**, 1128 (1847–48).

[51] W. Crum, *Ann.*, 62, 233 (1847); *Phil. Mag.*, **30**, 426 (1847).

[52] J. H. Gladstone, *Phil. Mag.*, **31**, 519 (1847).

[53] P. Schützenberger, *Ann chim. phys.*, [4], **21**, 235 (1870).

[54] A. P. N. Franchimont, *Ber.*, **12**, 1938 (1879); *Rec. trav. chim.*, **18**, 472 (1899).

[55] Z. H. Skraup, *Ber.*, **32**, 2413 (1899).

[56] C. F. Cross and E. J. Bevan, *Cellulose*, 1st ed., Longmans, Green & Co., London, 1895, p. 38. These authors considered for years that the most highly substituted cellulose acetate contained four acetyl groups for each glucose residue.

[57] G. W. Miles, U. S. Patent 838,350 (Dec. 11, 1906); through *Chem. Abstracts*, **1**, 653 (1907).

[58] A Girard, *Ann. chim. phys.*, [5], **24**, 337 (1881).

powder. When the latter was suitably dried *in vacuo,* it invariably had a composition close to that of $(C_6H_{10}O_5)_2.H_2O$ and Girard accordingly named it hydrocellulose. The notable research of Witz[59] started with the observation that certain bleached cottons contained many minute holes, the edges of which discolored on gentle heating and adsorbed certain dyestuffs intensely. Witz proved that such damage was caused by the adventitious adherence of solid calcium hypochlorite dust to the moist fabric. A clever use of dyestuffs then enabled him to eliminate local acidity, leading to hydrocellulose, as a cause of the damage, while elementary analyses showed that the hypochlorite functioned not as a chlorinating but as an oxidizing agent. The friable, overbleached calico was accordingly named oxycellulose.[60] Increased affinity for methylene blue and many other dyestuffs increased copper-reducing power and decreased mechanical strength, then formed criteria by means of which Witz was able to classify as oxidations other phenomena which troubled the textile trade. These oxidations included catalytic effects such as those with sunlight and air: sunlight, air, and iron salts: alkali and air; vanadium and chlorates; as well as more obvious ones with permanganates and dichromates in solutions of varying acidity.

Concurrently with the above work, structural organic chemistry in general was being built up with brilliant success by arguments based on the analyses of substances which were chemical individuals. But cellulose and its derivatives were generally fibrous, insoluble materials which had no sharp melting or boiling points and which gave negative or indefinite results in molecular-weight determinations. Deprived of the usual criteria of homogeneity and purity, investigators in the cellulose field very frequently made the mistake of assuming these qualities in their preparations on insufficient evidence and accordingly attached molecular meanings to their analytical data. As the composition of mixtures naturally varied with the details of the individual preparation, a confusion of divergent formulas was applied to products obtained by essentially the same means, and the originator of each formula insisted on exact adherence to a special set of conditions. The varying percentage of water in hydrocellulose led to formulas ranging from $(C_6H_{10}O_5)_2 \cdot H_2O$ to $(C_6H_{10}O_5)_6 \cdot H_2O$,[61–63] until it was shown that proper washing and thorough drying resulted in the empirical formula $C_6H_{10}O_5$.[64,65] The latter composition was eventually adopted for regenerated cellulose (viscose) and for Mercer's cellulose hydrate,[66] which differed from hydrocellulose in having a much smaller copper-reducing power.[61] Although Franchimont's acetylation studies[67] quickly made him suspect that Witz's original oxycellulose specimens contained much unchanged cellulose, it became customary for years to attach empirical formulas to oxycelluloses prepared by different methods.[68] The extensive work of Berl and Klaye[69] did much to demonstrate the irreproducibility of the analytical data. Hess[70] showed that oxycelluloses had substantially the same optical rotation in cuprammonium as cellulose itself, and the more general studies of Hibbert and Parsons[71] and Heuser and Stöckigt[72] demonstrated the heterogeneous nature of the oxidations.[71,73]

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[59] G. Witz, *Bull. soc. ind. Rouen,* **11,** 169 (1883); **12,** 638 (1883). Extensive abstracts in *Dinglers Polytech. J.,* **250,** 271 (1883).

[60] Witz restricted the term to material preserving the physical appearance and insolubility of the original fibers and called the more highly reducing, alkali-soluble by-product of the oxidations "celluloglucose." The latter corresponded in properties to the nitric acid oxycellulose described a few months later by Cross and Bevan, *J. Chem. Soc.,* **43,** 22 (1883).

Structural ideas concerning the esters of cellulose underwent analogous modifications. Attempts to represent the lower nitrates by formulas varying from $C_{24}H_{36}O_{16}(NO_3)_4$ to $C_{24}H_{28}O_8(NO_3)_{12}$,[74] or even by similar formulas based on a C_{48} unit,[75] were gradually abandoned with the recognition that the nitration reaction was an equilibrium governed by the amount of water in the spent nitrating liquor[51,69] and complicated by the formation of hydro- and oxy-cellulose nitrates.[69] Similar complications, together with uncertainty about the reliability of acetyl analyses, delayed the general acceptance of the triacetyl, rather than the tetraacetyl,[56] derivative as the most highly substituted cellulose acetate until 1906.[53,76] Representations of the sulfuric acid ester salts as $C_{10}H_{20}O_2(SO_3)_2 . BaO . 2H_2O$[77] and analogous formulas were later shown to have no validity.[78] Finally, in 1936, the variable composition of the xanthate esters was fully recognized by Lieser and Leckzyck.[79]

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[61] C. G. Schwalbe, *Z. angew. Chem.*, **20**, 2166 (1907)

[62] H. Ost, *Z. angew Chem.*, **19**, 993 (1906).

[63] G. Büttner and J. Neuman, *Z angew. Chem.*, **21**, 2609 (1908).

[64] A. L. Stern, *J. Chem. Soc.*, **85**, 336 (1904).

[65] H. Ost, *Ann.*, **398**, 313 (1913).

[66] H. Ost and F. Westhoff, *Chem.-Ztg.*, **33**, 197 (1909).

[67] A. P. N. Franchimont, *Rec. trav. chim.*, **2**, 241 (1883).

[68] C. G. Schwalbe, *Die Chemie der Cellulose*, Gebrüder Borntrager, Berlin, 1911, pp. 129–44, 160–262 Gives an extensive account of early hydrocellulose, cellulose hydrate, and oxycellulose researches.

[69] E. Berl and R. Klaye, *Z. ges. Schiess- u. Sprengstoffw.*, **2**, 381, 403 (1907); through *Chem. Abstracts*, **2**, 184, 898 (1908).

[70] K. Hess, *Z. angew. Chem.*, **37**, 993 (1924).

[71] H. Hibbert and J. L. Parsons, *J. Soc. Chem. Ind.*, **44**, 473T (1925). This article contains an excellent review of the literature.

[72] E. Heuser and F. Stöckigt, *Cellulosechemie*, **3**, 61 (1922).

[73] P. H. Clifford and R. G. Fargher, *Shirley Inst. Mem.*, **1**, 118 (1922); *J. Textile Inst*, **13**, T189 (1922). A comprehensive review.

[74] J. M. Eder, *Ber.*, **13**, 169 (1880). A table of earlier formulas is included

[75] D I. Mendeleev, *Mon. sci.*, p. 510 (1897); quoted by G Lunge and J. Bebié, *Z angew. Chem.*, **14**, 483 (1901)

Although the enormous mass of research so briefly catalogued above was in many respects of permanent value to industry, the data as a whole served to confuse rather than clarify the structural chemistry of cellulose. The truth of this statement is seen in the diversity of formulas suggested for cellulose and by the hesitation with which each suggestion was advanced by its sponsor. The merits and demerits of the following proposals have been carefully discussed by Hibbert.[80]

Structures II and III were considered to explain the 26% yield of ω-bromo-furfuraldehyde obtained from cellulose by hydrogen bromide in chloroform.[81] Cross and Bevan formulas such as II were also unique in their claim that the hexose unit in cellulose was more closely related to a keto sugar than to glucose and that these units contained four, rather than three, hydroxyl groups capable of being acetylated. Various modifications of the tannin-like model VI ("celluxose") assumed 3.3 to 3.1 hydroxyl groups, gave special consideration to the yields of cellobiose octaacetate recovered in the acetolysis of cellulose, and recognized that the glycoside linkage was very common in nature. Barthelemy's more complicated unit V contained ethylene oxide rings which were supposed to add on the elements of caustic soda during the preparation of alkali cellulose. A similar argument, together with the existence of cellobiose, had led Vieweg[82] to another anhydrodisaccharide ($C_{12}H_{20}O_{10}$) structure, polymerized in an unknown way. The composition of various cellulose nitrates also made Eder[83] favor much the same conclusion. Vignon (Structure I) was particularly interested in the reactions of oxycellulose, while Pictet and his collaborators later supported the same formula because crystalline β-glucosan (I, $n = 1$) was produced by distilling starch or cellulose destructively at 210°C. and 10 mm.[84]

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[76] H. Ost, *Z. angew. Chem.*, **19**, 993 (1906).

[77] M. Hönig and S. Schubert, *Monatsh.*, **6**, 708 (1885). These authors recognized that the cellulose was degraded.

[78] A. L. Stern, *J. Chem. Soc.*, **67**, 74 (1895). A good review is included.

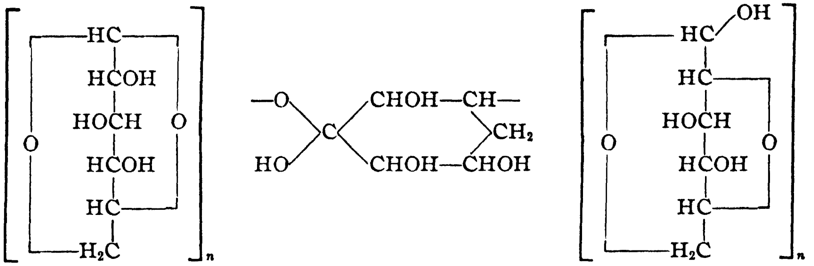
[79] T. Lieser and E. Leckzyck, *Ann.*, **522**, 56 (1936).

[80] H. Hibbert, *Ind. Eng. Chem.*, **13**, 256, 334 (1921).

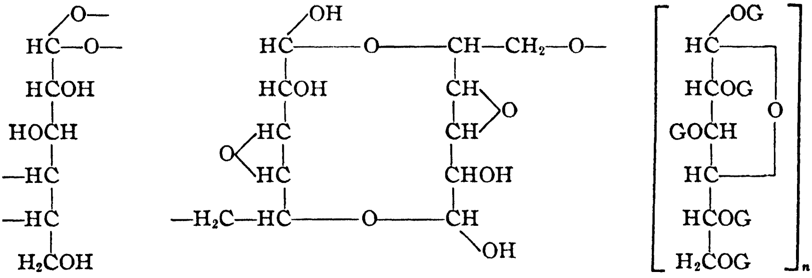
[81] H. J. Fenton and M. Gostling, *J. Chem. Soc.*, **79**, 361 (1901)

[82] W. Vieweg, *Ber.*, **40**, 3876 (1907).

[83] J. M. Eder, *Ber.*, **13**, 176 (1880).



I. Vignon,[85] Pictet[86-88]   II. Cross and Bevan[89]   III. Green[90,91]



IV. Tollens[92]   V. Barthelemy[93]   VI. Hess[94]

Some Early Formulas Proposed for Cellulose

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[84] Formula I was conclusively disproved by J. C. Irvine and J. W. Oldham (*J. Chem. Soc.*, 119, 1744 (1921); 127, 2903 (1925)), who methylated β-glucosan and dextrins derived from it by heating with zinc chloride. R. J. Dimler, H. A. Davis, and G. E. Hilpert (*J. Am. Chem. Soc.*, 68, 1377 (1946)) later found that the isomeric D-glucosan $< 1,4 > \beta < 1,6 >$ was formed in smaller amount during the destructive distillation, but its structure is also irrelevant to that of cellulose.

[85] L. Vignon, *Bull. soc. chim.*, [3], 22, 597 (1899).

[86] A. Pictet and J. Sarasin, *Helv. Chim. Acta*, 1, 87 (1918).

[87] A. Pictet and M. Cramer, *Helv. Chim. Acta*, 3, 640 (1920).

[88] A. Pictet and J. H. Ross, *Helv. Chim. Acta*, 5, 876 (1922).

[89] C. F. Cross and E. J. Bevan, *J. Chem. Soc.*, 79, 366 (1901). See also *Researches on Cellulose, 1895–1900*, p. 77; *1900–1905*, p. 102; and *Cellulose*, 1st ed., 1895, Longmans, Green & Co., London, p. 75.

[90] A. G. Green, *Z. Farben- u. Textilchem.*, 3, 97 (1904).

[91] A. G. Green and A. G. Perkin, *J. Chem. Soc.*, 89, 811 (1906).

[92] B. Tollens, *Kurzes Handbuch der Kohlenhydrate*, Vol. 2, E. Trewendt, Breslau, 1895, p. 252.

[93] H. Barthelemy, *Caoutchouc & gutta-percha*, 14, 9274 (1917); through *Chem. Abstracts*, 11, 3428 (1917).

[94] K. Hess and W. Wittelsbach, *Z. Elektrochem.*, 26, 232 (1920); K. Hess, *Helv. Chim. Acta*, 3, 866 (1920). G in formula is a glucosyl group.

All authorities recognized that the physical properties of cellulose and its solutions indicated a molecular weight far greater than that of a single glucose residue. Formulas II, IV, and V expressed this fact by conventional main-valence linkages of a type that was broken by acid hydrolysis. Formulas I, III, and VI, on the other hand, were self-contained from the main-valence point of view and their originators attributed the high molecular weight of cellulose to "association" between secondary valence forces analogous to those holding individual atoms of silver in place in the colloidal particle,[94] or to "physical aggregates" such as are constantly found occurring in the case of colloidal substances.[91] This tendency to stress the colloidal aspect of cellulose was occasionally carried to the point of denying that the methods of classical organic chemistry would ever assign a definite structure to the polysaccharide.[95]

On looking backward through the decades from the vantage point of the present, it is easy to see that the structural chemistry of cellulose remained at a virtual standstill from 1860 to 1920 because ancillary sciences, indispensable to a solution of the problem, were in an undeveloped condition. By 1920, the labors of Emil Fischer and other investigators had placed the chemistry of the simple sugars upon a solid foundation.[96] The methylation method of determining the position of hydroxyl groups in the carbon skeleton completed its long apprenticeship, in the hands of Purdie, Irvine, Denham and Woodhouse, and others, about the same time, and the essential, partly methylated glucoses had been prepared and characterized.[97] X-rays gave the first clear diffraction pattern of fibrous cellulose in 1920,[23] and shortly thereafter the colloid chemistry of linear macromolecules, such as cellulose proved to be, was very greatly clarified by Staudinger and his collaborators.[98] These events make it convenient to choose the year 1919, when Emil Fischer died, as the beginning of the modern period of cellulose chemistry.

3. Rise and Decline of the Association Theory

Much of the doubt surrounding the structure of cellulose was swept away at one stroke when almost completely methylated cotton was degraded in very good yield to the well-characterized, crystalline 2,3,6-trimethylglucose.[99,100] This result demonstrated that hydroxyl groups occupied the second, third, and sixth positions of each anhydroglucose unit in cellulose. All of the older formulas for the polysaccharide were invalidated except a suggestion of Hibbert's (Structure VII)[80] which was based on preliminary methylation data and in part upon the relative ease of formation and conversion displayed by five- and six-membered cyclic acetals. The adoption of the pyran ring structure for the more stable type of glucosides,[101,102] together with the demonstration that cellobiose was a 4-glucopyranosylglucose,[103,104] then made it reasonable to regard cellulose as essentially a linear macromolecule[105–107] in which uniform and equivalent main-valence glucosidic links unite a large number of hexose units (Structure VII). This view is universally accepted today, and all other sections of this text are devoted to expounding it. The point of immediate interest is that in the early 1920's the proponents of Formula VII were unable to adduce convincing proof in its support. Their failure in this respect permitted an alternative interpretation of the facts to gain much ground and to stimulate a large volume of research.

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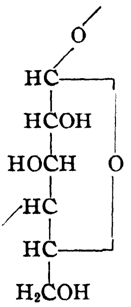
[95] C. F. Cross and E. J. Bevan, *Researches on Cellulose, 1900–1905*, Longmans, Green & Co., London, pp. 1–7.

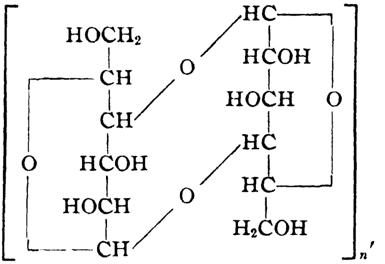
[96] C. S. Hudson, *J. Chem. Education*, **18**, 353 (1941).

[97] J. C. Irvine, *J. Chem. Soc.*, **123**, 898 (1923).

[98] H. Staudinger, *Die hochmolekularen organischen Verbindungen*, J. Springer, Berlin, 1932.



VII (repeat *n* times for main-valence molecule)



VIII (when main-valence molecule has x = 2 anhydroglucose units)

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[99] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **123,** 518 (1923).

[100] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **103,** 1735 (1913); **105,** 2357 (1914).

[101] E. L. Hirst, *J. Chem. Soc.*, **1926,** 350.

[102] W. Charlton, W. N. Haworth, and S. Peat, *J. Chem. Soc.*, **1926,** 89.

[103] G. Zemplén, *Ber.*, **59B,** 1254 (1926).

[104] W. N. Haworth, C. W. Long, and J. H. G. Plant, *J. Chem. Soc.*, **1927,** 2809.

[105] This name was coined by H. Staudinger and J. Fritschi, *Helv. Chim. Acta,* **5,** 785 (1922).

[106] H. Staudinger, *Ber.*, **53B,** 1081 (1920).

[107] K. Freudenberg, *Ber.*, **54B,** 767 (1921).

The physical properties of fibrous cellulose and of its solutions had created a deep-seated feeling that the polysaccharide was essentially a colloidal substance.[108] Unfortunately for the study of cellulose and other high polymers, most of the spectacular early successes of colloid chemistry did not concern linear macromolecules but were obtained with atoms or small molecules which assembled in regular array to form aggregates of colloidal size. The forces responsible for such aggregation were clearly of the residual or secondary valence type active in the molecular lattice of a crystal or between the molecules of a fatty acid associated in a nonpolar solvent like benzene. These suspensoid, association, or micellar[109] colloids included aqueous sols of many metals, of dyestuffs like indigo, and of soaps in the sol, gel, and curd form. The micellar structure of the soaps was the subject of particularly intensive studies by McBain and his collaborators.[110,111] These systems resembled solutions of cellulose and its derivatives in the unexpectedly minute values they displayed in osmotic pressure and similar determinations, in their abnormal viscosity phenomena, and in the erratic and apparently capricious way the quantitative data depended on the previous history of the specimen and on the experimental details. *A priori*, it was indeed reasonable to argue, as Vignon, Green, and Hess had done (Structures I, III, and VI), that cellulose was similarly constituted. Only a few anhydroglucose units were assumed to be united by main valences to give a nonreducing $(C_6H_{10}O_5)_x$ molecule, large numbers, n', of which then associated to a physical aggregate whose average size was greatly dependent on the physicochemical environment. Formula VIII represents the case in which x is two and the true chemical molecule is chosen to satisfy the methylation data. Although the nature of the forces holding such main-valence molecules in aggregates always remained obscure, it was supposed that they resembled those responsible for soap micelles or for the coordination complexes so convincingly explained by Werner.[112-114] The word "polymerization" lost its precision for a few years because some writers extended its meaning to include the concept of "association" or "aggregation"[115,116] while others did not.[98,117] In the same way, "molecular weight" was not infrequently confused with "particle" or "micellar" weight.[118]

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[108] C. G. Schwalbe, *Die Chemie der Cellulose*, Gebrüder Bornträger, Berlin, 1911, p. 356, reviewed the earlier work.

[109] "Micelles" were originally the submicroscopic crystallites whose presence in fibrous cellulose was inferred by Nägeli.

[110] M. E. Laing and J. W. McBain, *J. Chem. Soc.*, **117**, 1506 (1920).

[111] J. W. McBain, *J. Phys. Chem.*, **30**, 239 (1926).

[112] A. Werner, obituary, *J. Chem. Soc.*, **117**, 1639 (1920). Biography by P. Peiffer, *J. Chem. Education*, **5**, 1090 (1928).

[113] N. V. Sidgwick, Presidential Address, Section B, *Brit. Assoc. for the Advancement of Science Reports*, Spottiswoode Ballantyne & Co., London, 1927, p. 27.

[114] M. Bergmann, *Ber.*, **59B**, 2973 (1926).

The association theory also appeared to be supported by experimental evidence in other fields, for it was known that the destructive distillation of rubber yielded isoprene and that isoprene, with suitable catalysts, gave back a rubber-like material. Starch, too, was changed by *Bacillus macerans* to a mixture of the Schardinger dextrins, which were nonreducing crystalline substances with apparent molecular weights of from two to eight anhydroglucose units,[119,120] but now known to contain six or seven such units in a ring.[121] When applied to cellulose, the theory not only provided plausible although *ad hoc* explanations of the physical properties of the solutions but was compatible with x-ray and optical data obtained from the solid fiber (see Chapter IV). These data indicated that much of the fiber consisted of crystallites or micelles of colloidal dimensions and that each x-ray unit cell contained only a small number of glucose residues.[122-124] While Structure VII had to be of great length in order to explain the experimental failure to find units corresponding to the ends, Structure VIII required no additional assumptions in this respect. Supported by this series of arguments, many chemists came to believe that suitable solvents or chemical reagents might "depolymerize" cellulose to small, main-valence molecules of a kind which would readily revert to aggregates of colloidal size. Several well-known textbooks were written from this point of view.[1,115,116] It is now necessary to record some of the fruitless attempts that were made to support these ideas experimentally.

The first emphatic rejections of the macromolecular theory came from

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[115] See, for example, H. Pringsheim, *The Chemistry of the Monosaccharides and of the Polysaccharides*, McGraw-Hill, New York, 1932.

[116] See for example, P. Karrer, *Polymere Kohlenhydrate*, Akadem. Verlagsgesellschaft, Leipzig, 1925.

[117] See, for example, K. Hess, *Die Chemie der Zellulose*, Akadem. Verlagsgesellschaft, Leipzig, 1928, p. 576.

[118] The colloidal aspects of the macromolecular and association theories were ably reviewed by H. Staudinger, *Kolloid-Z.*, **53**, 19 (1930). See also H. Staudinger, K. Frey. R. Signer, W. Starck, and G. Widmer, *Ber.*, **63B**, 2308 (1930).

[119] H. Pringsheim and F. Eissler, *Ber.*, **46**, 2959 (1913).

[120] P. Karrer and C. Nägeli, *Helv. Chim. Acta*, **4**, 169 (1921).

[121] D. French and R. E. Rundle, *J. Am. Chem. Soc.*, **64**, 1651 (1942).

[122] K. H. Meyer and H. Mark, *Ber.*, **61B**, 593 (1928).

[123] H. Mark, *Ber.*, **59B**, 2982 (1926), reviewed the earlier x-ray results.

[124] M. Polanyi, *Naturwissenschaften*, **9**, 337 (1921).

Hess and from Karrer. Karrer and his collaborators[125,126] determined the heats of combustion of several compound sugars, $(C_6H_{10}O_5)_n.H_2O$, where n was 2 to 4, and noted that the values increased to that of β-glucosan, $C_6H_{10}O_5$. Starch, various crystalline starch dextrins, and cellulose had the same heat of combustion as β-glucosan. This result indicated either that n' was unity in Structure VIII or that the Chain VII contained a large number of units (more than sixty). The latter alternative was rejected as highly improbable, and the association hypothesis was considered to have received decisive support. A little previously, Hess and his collaborators[127] had discovered that the specific rotation of cellulose dissolved in a caustic soda–cuprammonium solution reached a maximum when one atom of copper was present for each glucose residue. This rotation was independent of the origin of the cellulose, provided no other polysaccharide was present, and was also independent of the concentration, provided the latter was above a certain minimum value. A glucosan structure was assumed for cellulose because, in this event, the formation of the copper complex obeyed the mass action law. The fact that the data were also consistent with a sufficiently long chain of anhydroglucose units seems to have been ignored. Traube,[128] as well as Neale,[129] also discussed the supposed constitution of the cellulose–copper–alkali complex in detail.

Hess and his collaborators were very successful in obtaining ramie cellulose,[130] cellulose triacetate,[131] trimethyl- and triethyl-cellulose,[132,133] and an acetone–cellulose nitrate complex[134] in crystalline form. In each case some acidic pretreatment was involved, and today the formation of such micro or semimicro, rather soft crystals is recognized as a typical characteristic of linear macromolecules of intermediate chain length.[135] The phenomenon, however, was claimed by Hess as evidence for the anhydroglucose Structure VIII on the ground that colloidal aggregates were not likely to crystallize.

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[125] P. Karrer, C. Nägeli, O. Hurwitz, and A. Wälti, *Helv. Chim. Acta*, **4**, 678 (1921).

[126] P. Karrer, *Ber.*, **55B**, 2854 (1922).

[127] K. Hess, W. Weltzien, and E. Messmer, *Ann.*, **435**, 1 (1924).

[128] W. Traube, *Ber.*, **54B**, 3220 (1921); **55B**, 1899 (1922); **56B**, 268, 1653 (1923).

[129] S. M. Neale, *J. Textile Inst.*, **16**, T363 (1925).

[130] K. Hess and G. Schultze, *Ann.*, **456**, 55 (1927).

[131] K. Hess, G. Schultze, and E. Messmer, *Ann.*, **444**, 266 (1925); K. Hess, *Z. angew. Chem.*, **37**, 999 (1924).

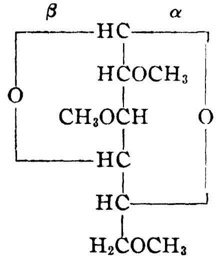
[132] K. Hess and H. Pichlmayr, *Ann.*, **450**, 29 (1926).

[133] K. Hess and A. Müller, *Ann.*, **455**, 205 (1927).

[134] K. Hess, C. Trogus, and K. Dziengel, *Ann.*, **501**, 49 (1933).

[135] W. H. Carothers and J. W. Hill, *J. Am. Chem. Soc.*, **54**, 1559 (1932).

Another argument for the association theory was found in the physical behavior of dilute solutions of cellulose and its derivatives in glacial acetic acid, phenol, and other solvents. The observed small depressions in freezing point fluctuated capriciously as the solutions aged and frequently corresponded to molecular weights of one or a few anhydroglucose units. All these data were interpreted as caused by the partial or complete dissociation of associated complexes and by their spontaneous reversion to a more highly aggregated state.[127,136–138] Although similar depressions were observed by others, the interpretation was not accepted because the values were found to fluctuate erratically instead of varying uniformly as the Hess theory demanded.[139,140] Molecular weights were then determined by isothermal distillation through a porous plate,[141–143] and it was found possible later to eliminate the disturbing influence of the plate.[144–146] Today there is a tendency to concede that some of the effects observed by Hess and his collaborators are real and of great interest because they occur with numerous macromolecular materials. The isothermal distillation data appear, however, to have been of inadequate precision to have justified the conclusions drawn.[147] Staudinger and Schulz[148] concluded



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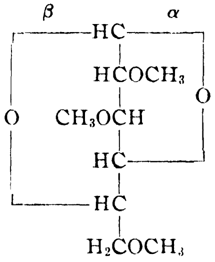

X

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[136] K. Hess and G. Schultze, *Ann.*, **448**, 99 (1926).

[137] K. Hess and H. Friese, *Ann.*, **450**, 40 (1926).

[138] K. Hess and G. Schultze, *Ann.*, **455**, 81 (1927).

[139] M. Bergmann, E Knehe, and E Lippmann, *Ann.*, **458**, 93 (1927)

[140] K. Freudenberg and E. Braun, *Ann.*, **460**, 288 (1928).

[141] M. Ulmann, *Z. physik. Chem.*, **A156**, 419 (1931).

[142] M. Ulmann and K. Hess, *Ber* , **66B**, 495 (1933).

[143] K. Hess and M. Ulmann, *Ann.*, **504**, 81; *Ber.*, **67B**, 2131 (1934).

[144] K. Hess and M. Ulmann, *Ber.*, **69B**, 1448 (1936).

[145] M. Ulmann, *Angew. Chem.*, **49**, 926 (1936).

[146] M. Ulmann, *Ber.*, **69B**, 1437 (1936).

[147] K. Hess and L. A. Surânyi, *Z. physik. Chem.*, **A184**, 321 (1939).

[148] H. Staudinger and G. V. Schulz, *Ber.*, **70B**, 1577 (1937); see also numerous similar comments by other authors.

that such depressions of freezing point and of vapor pressure were anomalous phenomena which gave no clue to the true weight of a macromolecular solute (see Chapter X-B).

If the association hypothesis was correct, one or other of the anhydro derivatives of 2,3,6-trimethylglucose should be capable of a reversible transformation to trimethyl cellulose. Various methods of preparing these anhydrides led to conflicting results,[140,149–152] but in the end it appeared that only one of the two possibilities IX and X had been synthesized and that the very highly strained ring structure of the other made its existence unlikely. The 2,3,6-trimethylglucosan <1,4> <1,5> was a mobile, colorless oil, b. p., 83–85°/0.1 mm., that had the normal properties and showed no tendency to change into trimethyl cellulose.[140] As an isomeric trimethylhexose anhydride with the required potentiality has not yet been isolated, this attempt to support the association theory was inconclusive.

Another obvious line of work was to change cellulose to the hypothetical glucosan required by Structure VIII ($x = 1$). Acetyl chloride in the presence of a trace of moisture dissolved cotton, and a chlorine-free cellulose acetate A was isolated in 90% yield.[127] Although this acetate gave apparent molecular weights of 2000 to 3000 in dilute phenol solution, its other properties, together with those of its derivatives, show it to be merely slightly degraded cellulose acetate. The action of hydrogen bromide in acetyl bromide on the acetate of cellulose A, followed by deacetylation in moist chloroform-ether, was reported to give a nearly quantitative yield of a crystalline "celloglucosan," $C_6H_{10}O_5 \cdot H_2O$.[127] An attempt to repeat this preparation, however, resulted not in "celloglucosan" but in a reputed anhydrotrihexosan which was first isolated as the crystalline nonaacetate and was considered to be the trimer of the expected compound.[153] Although this nonaacetate, on methylation and hydrolysis, gave a good yield of 2,3,6-trimethylglucose, its high specific dextrorotation of 86.6°, when contrasted with the small rotation of cellulose triacetate, rendered its relationship to the latter very questionable.

The dissolution of cotton in acetic anhydride and sulfuric acid was likewise considered to give a 90% yield of a crystalline "biosan" hexaacetate with an apparent molecular weight of 568 to 700 in sufficiently dilute acetic acid or phenol solution.[137,154] It was later shown, from the specific vis-

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[149] F. Micheel and K. Hess, *Ber.*, **60B**, 1898 (1927).

[150] K. Hess and F Micheel, *Ann* , **466**, 100 (1928).

[151] K. Hess and O. Littmann, *Ber.*, **66B**, 774 (1933).

[152] K. Freudenberg and E. Braun, *Ber.*, **66B**, 780 (1933)

[153] F. Micheel, *Ann.*, **456**, 69 (1927).

[154] K. Hess, *Ber.*, **54B**, 2867 (1921)

cosity,[155] the copper-reduction and acetyl values,[156] and the revised molecular weight,[157] that this "biosan" was really a mixture averaging about twelve glucose residues to the main-valence molecule. Further work by Hess and his collaborators resolved the "biosan" fractions into crystalline "limit" dextrins I and II and a cellulose acetate II.[158] The trinitrate of the dextrin II gave with acetone a crystalline addition complex. X-ray data from the latter were considered to prove identity of the "limit" dextrin with native cellulose, the examination of which was complicated by its biological character and by the assumed presence of interpenetrating, morphological films of a noncellulose nature (*Fremdhautsystem*).[159,160] The existence of these films has not been confirmed.

One of the corollaries of the "glucosan" theory was that copper-reducing derivatives like hydrocellulose or cellobiose were secondary products of little constitutional significance for cellulose. This inference was not accepted by the majority of those who adhered to the association theory. Very extensive work, particularly by Ost,[65] had set the maximum obtainable recovery of cellobiose octaacetate at 42–43%[161] and, since about one-third was degraded to glucose pentaacetate during the acetolysis, the original formation did not exceed 67% of the theoretical amount.[162,163] Although this result was compatible with the random breakdown of a uniformly linked, linear macromolecule[162,164] under the action of inorganic acid, it stood in stimulating contrast to the nearly quantitative yields of maltose often obtainable from starch by a vital agent like the enzyme diastase. As a result of some studies with phosphorus pentabromide, Karrer[165] suggested that both starch and cellulose were associated complexes based on a "cellosan" in which the glucosidic links united the 1,6- and the 1,4-positions of the two anhydroglucose units. Although hydrolysis of the 1,6-linkage gave cellobiose, the independent but concurrent scission of the 1,4-linkage would not do so and the yield of cellobiose would not be quantitative. This suggestion was abandoned because the "cellosan" structure, on methylation and hydrolysis, would have given 2,3,6- and 2,3,4-trimethylglucose in equimolecular amount, instead of 100% of the former.[99] The name "cellosan" was afterward adopted by Pringsheim and his collaborators[166] for a reputed anhydroglucose triacetate prepared by heating cellulose triacetate in naphthalene at 235°C. This work was shown to be erroneous.[167]

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[155] H. Staudinger and H. Freudenberger, *Ber.*, **66B**, 76 (1933).

[156] K. Freudenberg, *Ber.*, **62B**, 383 (1929).

[157] M. Bergmann and H. Machemer, *Ber.*, **63B**, 316 (1930).

[158] K. Dziengel, C. Trogus, and K. Hess, *Ann.*, **491**, 52 (1931).

[159] K. Hess, C. Trogus, and K. Dziengel, *Ann.*, **501**, 49 (1933).

[160] K. Hess, *Naturwissenschaften*, **22**, 469 (1934).

[161] H. Friese and K. Hess, *Ann.*, **456**, 38 (1927), claimed a 50–51% yield of cellobiose octaacetate.

[162] K. Freudenberg, *Ber.*, **54B**, 767 (1921).

[163] P. Karrer and F. R. Widmer, *Helv. Chim. Acta*, **4**, 174 (1921).

[164] J. Böeseken, J. C. Berg, and A. H. Kerstjens, *Rec. trav. chim.*, **35**, 320 (1916)

[165] P. Karrer and A. P. Smirnoff, *Helv. Chim. Acta*, **5**, 187 (1922).

Bergmann and Knehe,[168] in their acetolysis of cellulose with hydrogen chloride as a catalyst, isolated what they considered was the crystalline tetraacetate of a "cellobiosan." Dilute solutions of this substance had the proper molecular depressions in some solvents and much lower ones, attributed to association, in others. The corresponding "cellobiosan" was insoluble in water but dissolved in alkali to give a yellow solution. There is no doubt that this "cellobiosan," like Hess and Friese's "biosan," was a degraded cellulose mixture with an average molecular weight much greater than they thought.

In the course of their studies on the acetolysis of cellulose with sulfuric acid as a catalyst, Ost and his collaborators[169,170] isolated a fraction which they regarded as a "celloisobiose or isocellobiose octaacetate" and which gave ordinary cellobiose octaacetate on rearrangement. On deacetylation, the "isocellobiose" crystallized with half a molecule of water and was a reducing carbohydrate with ordinary properties. Although Weltzien and Singer[171] supported the individuality of Ost's "isocellobiose," it was presumed to be a mixture by Hess,[172] was not encountered by Zechmeister and Tóth,[173] and was shown to be a mixture of cellobiose and a new, reducing trisaccharide, "procellose," by Bertrand and Benoist.[174] "Procellose" proved to be identical with the substance now called cellotriaose.[173] A second "cellotriose" prepared by Ost[175] was probably an impure sample of the same substance, the fully methylated derivative of which had previously been isolated in a nonhomogeneous condition by Irvine and Robertson.[176]

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[166] H. Pringsheim, J. Leibowitz, A. Schreiber, and E. Kasten, *Ann.*, **448**, 163 (1926).

[167] G. Schultze and K. Hess, *Ann.*, **450**, 65 (1926).

[168] M. Bergmann and E. Knehe, *Ann.*, **445**, 1 (1925).

[169] H. Ost and R. Prosiegel, *Z. angew. Chem.*, **33**, 100 (1920).

[170] H. Ost and G. Knoth, *Cellulosechemie*, **3**, 25 (1922).

[171] W. Weltzien and R. Singer, *Ann.*, **443**, 71 (1925).

[172] K. Hess, *Die Chemie der Zellulose*, Akadem. Verlagsgesellschaft, Leipzig, 1928, p. 502.

[173] L. Zechmeister and G. Tóth, *Ber.*, **64B**, 854 (1931).

[174] G. Bertrand and S. Benoist, *Bull. soc. chim.*, [4], **33**, 1451 (1923); [4], **35**, 58 (1924). See also W. N. Haworth, E. L. Hirst, and O. Ant-Wuorinen, *J. Chem. Soc.*, **1932**, 2368.

[175] H. Ost, *Z. angew. Chem.*, **39**, 1117 (1926).

[176] J. C. Irvine and G. J. Robertson, *J. Chem. Soc.*, **1926**, 1488.

The occurrence of a fully methylated anhydrotrisaccharide in Irvine and Robertson's mixture has not been confirmed.

Two other attempts to fit the experimental data to the association theory are worthy of record. Herzog and Jancke[177] suggested that cellulose was an anhydrotetrasaccharide (Structure VIII, $x = 4$), largely because the x-ray diffraction pattern of the fibers contained four glucose residues in the unit cell. Schorger,[178] principally concerned with the yields of cellobiose and the presumed isocellobiose obtained in acetolysis, put forward a cyclic anhydrotetrasaccharide formula in which the linkages were of an acetal rather than the usual glucoside type.

The failure of the adherents of Structure VIII to provide reproducible and decisive evidence in its support enhanced the attractiveness of the rival Formula VII, which had been favored throughout by many workers, including E. Berl, K. Freudenberg, W. N. Haworth, E. Heuser, R. Kuhn, H. Mark, K. H. Meyer, O. L. Sponsler, H. Staudinger, and R. Willstätter. General opinion was undecided in 1927,[179] but in the following years cellulose was degraded to a series of individual, crystalline fragments corresponding to $n = 3$ to $n = 5$ in Formula VII. The course of the degradation was proved to be in agreement with the random scission of equivalent bonds in a linear macromolecule.[180] It became possible to estimate the average molecular weights of such giant, main-valence structures by improved measurements of osmotic pressure, by viscosity effects,[98] and by the ultracentrifuge.[181] The change in outlook became practically unanimous in 1932, when Haworth and Machemer[182] isolated 0.6% of crystalline 2,3,4,6-tetramethylglucose from the hydrolysis products of a purified, carefully fractionated trimethyl cellulose. This scission product was the long-sought-for[183] end group corresponding to VII and its amount indicated a chain containing at least 100 to 200 anhydroglucose units. Organic chemists were thus brought into agreement with those who had claimed a somewhat similar chain length for cellulose on one interpretation of the x-ray data.[184,185]

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[177] R. O. Herzog and W. Jancke, *Z. angew. Chem.*, **34**, 385 (1921).

[178] A. W. Schorger, *Ind. Eng. Chem.*, **16**, 1274 (1924).

[179] W. N. Haworth in *Chem. Soc. Ann. Repts*, **24**, 81 (1927); **25**, 106 (1928).

[180] K. Freudenberg, *Tannin, Cellulose, Lignin*, J. Springer, Berlin, 1933, p. 105.

[181] T. Svedberg and J. B. Nichols, *J. Am. Chem. Soc.*, **49**, 2920 (1927), discuss proteins, not cellulose.

[182] W. N. Haworth and H. Machemer, *J. Chem. Soc.*, **1932**, 2270.

[183] Earlier searches had given doubtful or negative results. See K. Hess and W. Weltzien, *Ann.*, **442**, 46 (1925), and refs. 99, 100, and 140.

[184] See H. Mark, *Trans. Faraday Soc.*, **29**, 42 (1933), and ref. 122.

[185] H. Mark, *Physik und Chemie der Cellulose*, J. Springer, Berlin, 1932, p. 197.

The new physical methods, however, gave average molecular weights that were approximately tenfold greater, and there was a tendency to assume that the long-chain chemical entities "associated" or "aggregated" in solution to produce the still larger complexes found by physical measurements.[186] This assumption abruptly collapsed fifteen years ago when it was discovered that Haworth and Machemer's trimethyl cellulose had been degraded more extensively than had been thought possible during its preparation.[187,188] Although repetition of the work yielded no tetramethylglucose from native cotton, the macromolecular structure was now so firmly established that the negative result was generally regarded, not as support for Structure VIII, but as proof that the main-valence molecule of cellulose contained at least 700 anhydroglucose units (specifically anhydroglucosepyranose units). The last, basic divergence of opinion was thus resolved into the conclusion that cellulose was a linear macromolecule containing up to 3000 or 3500 units, that it dispersed to individual molecules in sufficiently dilute solutions, and that its physical properties were greatly influenced by a degradation too slight to be readily detected by the methods of organic chemistry.

It may seem at first sight surprising that the association theory retained its grip over the intellects of so many workers for so long a period. But it must be remembered that their intuition, although wrong in one dimension, was certainly right in two. Since the time when the thread-like nature of the cellulose molecule was placed beyond question, many researches have been concerned with the association and the interplay of the secondary valence forces that radiate laterally from the cellulose chain.

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[186] This tendency was criticized by H. Staudinger and H. Freudenberger, *Ann.*, **501**, 162 (1933).

[187] K. Hess and F. Neumann, *Ber.*, **70B**, 728 (1937).

[188] W. N Haworth, E. L. Hirst, L. N. Owen, S. Peat, and F. J. Averill, *J. Chem. Soc.*, **1939**, 1885.

B. CHAIN STRUCTURE

CLIFFORD B. PURVES

1. Quantitative Yield of Glucose from Cellulose

The first step in establishing the structure of cellulose was to demonstrate beyond doubt that the purest available form (cotton) yielded nothing but glucose when hydrolyzed. In order to carry conviction, it was necessary to recover the glucose, or a suitable derivative, in pure, crystalline condition and in nearly quantitative yield. Irvine and Soutar[1] attacked this problem by submitting cotton to acetolysis in the presence of a sulfuric acid catalyst. The highly degraded triacetates, together with an excess of methanol containing 0.5% of hydrogen chloride, were kept for 70 hrs. in sealed tubes at 100°C. This procedure simultaneously removed acetyl groups and completed the degradation of the cellulose to a crystalline mixture of methyl α- and β-glucopyranosides. The over-all recovery of the latter was 85% of theory and the identification was satisfactory. In the next attempt, Monier-Williams[2] used cold, 72% sulfuric acid to dissolve the cotton and completed the degradation to glucose by diluting the solution with much water and boiling under reflux for 15 hrs. A 90.7% yield of crystalline glucose was obtained. Finally, Irvine and Hirst,[3] reverting to the acetylation technique, prepared cellulose triacetate in more than 99% yield from cotton by using small amounts of chlorine plus sulfur dioxide as a catalyst.[4] Methanolysis gave the crystalline, equilibrium mixture of the methyl α- and β-glucosides with the proper optical rotation and melting-point range. The mixture accounted for 95.5% of the cellulose after the weight of the latter was corrected for moisture and ash. The furfural test for pentosans was negative and compounds other than methyl glucoside were not detected. This work was generally accepted as decisive proof that pure cellulose consisted exclusively of glucose residues.

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[1] J. C. Irvine and C. W. Soutar, *J. Chem. Soc.*, **117**, 1489 (1920). This article pointed out technical weaknesses in the earlier claims.

[2] G. W. Monier-Williams, *J. Chem. Soc.*, **119**, 803 (1921); cf. H. Ost and L. Wilkening, *Chem.-Ztg.*, **34**, 461 (1910); H. Frahm, *Ber.*, **74B**, 622 (1941); H. H. Schlubach and E. Lührs, *Ann.*, **547**, 73 (1941).

[3] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **121**, 1585 (1922).

[4] W. L. Barnett, *J. Soc. Chem. Ind.*, **40**, 8T (1921).

2. Nature of the Hydroxyl Groups in Cellulose

(a) NUMBER OF HYDROXYL GROUPS

The next lead in the structural study was contributed by Denham and Woodhouse[5,6] who discovered that cotton, alternately soaked in 15% caustic soda and in dimethyl sulfate, slowly acquired methyl ether groups. Improved technique, including the use of 30% in place of 15% alkali, enabled Irvine and Hirst[7] to prepare a cellulose ether containing 42–43% of methoxyl groups in twelve treatments. The yield was reduced, mainly by manipulative losses, to 70% of theory. They noted that six additional methylations failed to increase the methoxyl content and concluded that the maximum possible degree of methylation corresponded to a trimethyl ether (OCH_3, 45.6%). Many later researches improved the methylation procedure until today it is possible to prepare almost completely methylated cellulose (OCH_3, about 45%) in 90% yield in a few operations.[8–11] Although the analyses for methoxyl in most of the earlier preparations tended to be slightly low owing to the method of estimation,[12] it still does not seem possible to bring the methoxyl content right up to the theoretical value of 45.6% without producing some degradation.[13,14] Nothing eventuated, however, that threw doubt on the claim that the highest alkylated derivative was the trimethyl ether. This fact, in conjunction with the long-standing recognition that the highest acetate was a triacetate[15] and the highest nitrate a trinitrate,[16] showed beyond doubt that, on the average, cellulose contained three hydroxyl groups for each glucose residue (also

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[5] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **103**, 1735 (1913). The principle of this method was made generally available for the alkylation of carbohydrates by W. N. Haworth, *J. Chem. Soc.*, **107**, 8 (1915).

[6] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **105**, 2357 (1914).

[7] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **123**, 518 (1923).

[8] K. Hess and W. Weltzien, *Ann.*, **442**, 46 (1925).

[9] E. Heuser and N. Hiemer, *Cellulosechemie*, **6**, 101, 125, 153 (1925).

[10] K. Freudenberg and E. Braun, *Ann.*, **460**, 288 (1928).

[11] W. N. Haworth, E. L. Hirst, and H. A. Thomas, *J. Chem. Soc.*, **1931**, 821.

[12] F. Neumann, *Ber.*, **70B**, 734 (1937); K. Freudenberg and H. Boppel, *Ber.*, **70B**, 1542 (1937).

[13] P. Karrer and E. Escher, *Helv. Chim. Acta*, **19**, 1192 (1936).

[14] G. G. Johnston, *J. Am. Chem. Soc.*, **63**, 1043 (1941).

[15] H. Ost, *Z. angew. Chem.*, **19**, 993 (1906).

[16] W. Crum, *Ann.*, **62**, 233 (1847); *Phil. Mag.*, **30**, 426 (1847).

designated more specifically as the anhydroglucose unit or the anhydro-β-glucopyranose unit).

Denham and Woodhouse[6] had hydrolyzed a methylated cellulose (OCH_3, 24–26%) in 43% hydrochloric acid and had obtained a new trimethylglucose in about 10% yield. This important result was soon checked by Irvine and Hirst,[7] who degraded their trimethyl cellulose (OCH_3, 42–43%) in methanol containing 1% of hydrogen chloride at 100–130°C. for 100 hrs. The resulting sirup, on distillation under diminished pressure, gave a methyl trimethylglucoside in 91.5% yield, corrected for the slightly low methoxyl content of the trimethyl cellulose. Aqueous acid hydrolyzed the glucoside to the new crystalline trimethylglucose in a yield of 86%, which therefore corresponded to an over-all recovery of 78.7%. This result was considered to be a minimum value. Much experience with sugars showed that the introduction of the methyl ether group did not involve unforeseen alterations in molecular structure and that such groups remained in their original positions even under drastic conditions. It followed that in trimethyl cellulose three methoxyl groups were attached to each glucose residue and that hydroxyl groups occupied the corresponding positions in cellulose itself. Moreover, since only one of the isomeric trimethylglucoses had been obtained, each glucose residue had its hydroxyl groups in the same three positions. Obviously, the next problem was to determine these positions.

(b) POSITION OF HYDROXYL GROUPS

Denham and Woodhouse[6] noted that the new trimethylglucose failed to form a phenylosazone and correctly decided that the second position was occupied by a methoxyl group. Their conjecture that the sugar was substituted in the second, third, and sixth positions was subsequently confirmed by several arguments. Ruff and Ollendorff[17] had degraded lactose or (4-(β-D-galactopyranosyl)-D-glucopyranose (see Structure I on page 58, where R is the galactose residue) to a galactosyl-D-arabinose (II) that was still capable of forming a phenylosazone. The second position of the arabinose, corresponding to the third position of the original glucose unit, was therefore unsubstituted. When completely methylated lactose was hydrolyzed, one of the scission products was bound to be a trimethylglucose methylated in the second and third positions. Haworth and

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[17] O. Ruff and G. Ollendorff, *Ber.*, **33B**, 1798 (1900). G. Zemplén, *Ber.*, **59B**, 2402 (1926), improved the technique and extended the degradation to the galactosyl-D-erythrose III, which did not form an osazone because the second position was substituted

Leitch[18] showed that the trimethyl sugar derived from lactose was identical with that obtained from cellulose. Since the oxidation of the trimethylglucose with nitric acid gave a dimethylsaccharic acid (V) rather than a trimethyl one, Irvine and Hirst[19] had no difficulty in deducing that the other methoxyl group had occupied the terminal or sixth position. In accord with Irvine's system of nomenclature,[19] the trimethylglucose was indexed as the 2,3,6-isomer (IV). 2,3,6-Trimethylglucose occurred as fine needles, m. p. 122–123°C., and as short prisms, m. p. 92–93°C. The mutarotation in water was from $[\alpha]_D$ 90.2° to a final value of 70.5°, and from 117.7° to 88.6° in neutral methanol.[19]

More evidence in favor of this assignment was derived from the behavior of the sugar when dissolved in methanol containing 1% of hydrogen chloride. A complex change in optical rotation occurred at room temperature,[19] and when Schlubach and Bomhard[20] arrested the reaction near the minimum rotation, they isolated a levorotatory, sirupy mixture of methyl 2,3,6-trimethylglucosides (VI). Methylation, followed by hydrolysis of the glucosidic methoxyl group with mineral acid,[20,21] gave the well-known, liquid tetramethylglucose (VII).[22] When the solution of the trimethylglucose in the acid methanol was boiled, a crystalline, somewhat less levorotatory methyl glucoside (VIII) was produced[23] which, on methylation and hydrolysis, yielded the still better known, crystalline tetramethylglucose (IX).[24,25] These important results restricted the positions of the ring structures in the isomeric tetramethyl derivatives (VII) and (IX) to the 1,5- and 1,4-positions. When these ring structures were unambiguously determined by entirely independent methods worked out by Haworth, Hirst, and their collaborators,[26,27] independent proof was forthcoming that 2,3,6-trimethylglucose could produce both 1,4- or furanose derivatives (VI) and 1,5- or pyranose ones (VIII). In other words, unmethylated hydroxyl groups were present in the fourth and fifth positions of the glucose skeleton.

Irvine and Rutherford[28] synthesized 2,3,6-trimethylglucose from methyl

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[18] W. N. Haworth and G. C. Leitch, *J. Chem. Soc.*, **113**, 188 (1918).

[19] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **121**, 1213 (1922).

[20] H. H. Schlubach and H. Bomhard, *Ber.*, **59B**, 845 (1926).

[21] J. C. Irvine and R. P. McGlynn, *J. Am. Chem. Soc.*, **54**, 356 (1932).

[22] J. C. Irvine, A. W. Fyfe, and T. P. Hogg, *J. Chem. Soc.*, **107**, 524 (1915).

[23] H. H. Schlubach and K. Moog, *Ber.*, **56B**, 1957 (1923).

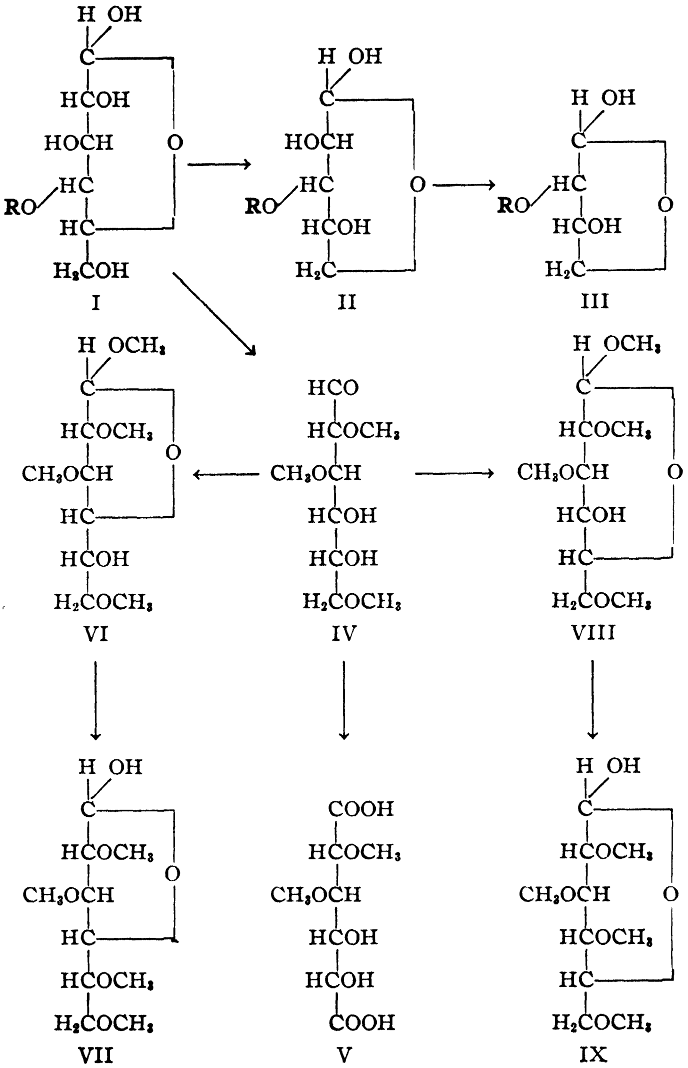
[24] W. N. Haworth and E. L. Hirst, *J. Chem. Soc.*, **119**, 193 (1921).

[25] T. Purdie and J. C. Irvine, *J. Chem. Soc.*, **85**, 1049 (1904).

[26] W. Charlton, W. N. Haworth, and S. Peat, *J. Chem. Soc.*, **1926**, 89.

[27] E. L. Hirst, *J. Chem. Soc.*, **1926**, 350.

[28] J. C. Irvine and J. K. Rutherford, *J. Am. Chem. Soc.*, **54**, 1491 (1932).



2,3-dimethyl-α-glucopyranoside, the structure of which was known because the corresponding sugar formed no phenylosazone and gave L(*dextro*)-dimethoxysuccinic acid on oxidation with nitric acid. Nitration of the glucoside gave methyl 2,3-dimethyl-4,6-dinitro-α-glucoside (methyl 2,3-dimethyl-α-glucoside-4,6-dinitrate) and a subsequent iodination, with sodium iodide in acetone at 100°C., resulted in methyl 2,3-dimethyl-4-nitro-6-iodo-

6-desoxy-α-glucoside (2,3-dimethyl-6-iodo-4-nitrate derivative). Replacement of the iodine atom by an acetate group, hydrolysis of the latter to hydroxyl, and methylation led to methyl 2,3,6-trimethyl-4-nitro-α-glucoside (methyl 2,3,6-trimethyl-α-glucoside-4-nitrate). Iron dust in acetic acid reduced the nitrate to an hydroxyl group; acid hydrolysis removed the glucosidic methoxyl group, and crystalline 2,3,6-trimethylglucose remained. The recognition of this trimethylglucose as the 2,3,6-isomer demonstrated that the glucose residues in cellulose were unsubstituted in the second, third, and sixth positions, as shown in Section A of this Chapter (III, Structure VII). This conclusion was supported by a direct method in 1937, when Jackson and Hudson[29] oxidized cellulose with aqueous periodic acid, a selective agent capable of cleaving glycols to two carbonyl functions.

$$R_1\text{—CHOH—CHOH—}R_2 + HIO_4 \longrightarrow R_1CH{=}O + R_2CHO + HIO_3.$$

Hydrolysis of the resulting "periodate oxycellulose," whose properties are discussed in Section C-3 of this Chapter III, yielded the glyoxal and D-erythrose to be expected from the oxidative scission of the unsubstituted 2,3-glycol unit in cellulose.

3. Nature of the Linkages between the Anhydroglucose Units

The allocation of the hydroxyl groups in cellulose to the second, third, and sixth positions of the anhydroglucose units left the mode in which the latter were linked together quite uncertain. The glucosidic bond might possess either the alpha or the beta configuration and might be attached to either the fourth or fifth position in the adjacent hexose unit. Denham and Woodhouse[30] were quick to realize that the latter alternative created doubt as to whether the hexose units possessed a 1,5- or 1,4-cyclic structure. In addition, the earlier x-ray data were erroneously held by Sponsler and Dore[31] to be consistent with a cellulose structure in which glucopyranose residues were united alternately by glucosidic 1,1- and by ether 4,4-oxygen linkages. The obvious way to clear up these uncertainties was to prepare and study scission products that were intermediate in complexity between cellulose and glucose. Cellobiose was the first of these products to be obtained in pure, crystalline form.

[29] E. L. Jackson and C. S. Hudson, *J. Am. Chem. Soc.*, **59**, 2049 (1937); **60**, 989 (1938).

[30] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **111**, 244 (1917).

[31] O. L. Sponsler and W. H. Dore, in *Fourth Colloid Symposium Monograph*, Chemical Catalog Co., New York, 1926, p. 174; through *Chem. Abstracts*, **21**, 3268 (1927).

(a) CELLOBIOSE

Hydrolysis of Cellulose to Cellobiose. The most advantageous method of preparing cellobiose octaacetate and, from it, the sugar itself,[32] is still based on the work of Franchimont,[33] who degraded cotton with acetic anhydride containing sulfuric acid. Skraup and König[34] demonstrated that Franchimont's crystals were the octaacetate of a new, reducing disaccharide consisting of two glucose residues and not fermented by yeast. The insensitivity toward yeast maltase, together with the ready hydrolysis to glucose brought about by emulsin,[35] showed that the disaccharide linking in cellobiose had the beta configuration. The methylation of Skraup and König's crystalline methyl heptaacetyl-β-cellobioside,[34] or of cellobiose itself,[24] gave the crystalline heptamethyl derivative[24,36] which, upon acid hydrolysis, produced 2,3,4,6-tetramethylglucopyranose and 2,3,6-trimethylglucose in equimolecular amount.[24] This result restricted the structural possibilities for cellobiose to either 4- or 5-β-glucopyranosylglucose.

The first attempt to remove this ambiguity was that of Zemplén,[37] who prepared the oxime of cellobiose and degraded it by standard methods to the glucosylarabinose (Structure II, where R is the glucose residue). A repetition of the process led in poor yield to a sirupy glucosylerythrose (III) from which an osazone was *not* obtained. The second position in the erythrose, corresponding to the fourth in the original glucose unit, was accordingly considered to be blocked by the disaccharide linkage. This negative evidence was given positive confirmation by the work of Haworth, Hirst, and their collaborators.[38] They eliminated the cyclic structure in the reducing half of cellobiose by oxidizing the disaccharide with bromine water to cellobionic acid. Complete methylation of the latter included the substitution of the position formerly occupied by the ring and resulted in octamethylcellobionic acid (X). Acid hydrolysis then gave a 92% yield of 2,3,4,6-tetramethylglucopyranose from the left-hand side of (X) and an

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[32] G. Braun, in *Organic Syntheses*, Collective Volume II, Wiley, New York, 1943, pp. 122, 124.

[33] A. P. N. Franchimont, *Rec. trav. chim.*, **18**, 472 (1899).

[34] Z. H. Skraup and J. König, *Monatsh.*, **22**, 1011 (1901).

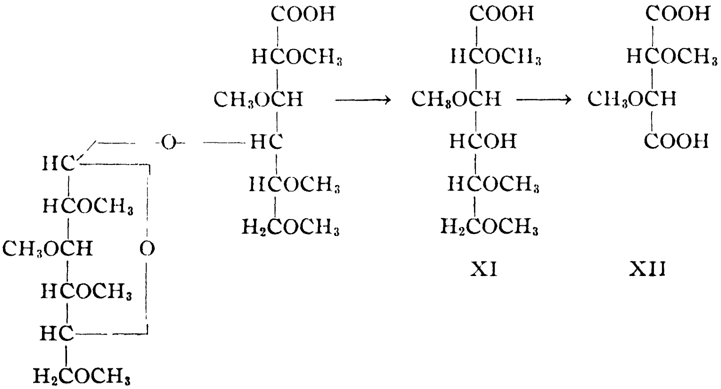
[35] E. Fischer and G. Zemplén, *Ann.*, **365**, 1 (1909); N. K. Richtmyer and C. S. Hudson, *J. Am. Chem. Soc.*, **61**, 1834 (1939).

[36] P. Karrer and F. Widmer, *Helv. Chim. Acta*, **4**, 174 (1921). A crystalline methyl hexamethyl-β-cellobioside was also described.

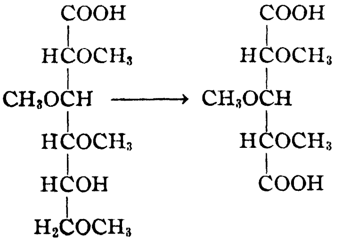
[37] G. Zemplén, *Ber.*, **59B**, 1254 (1926). See also A. M. Gakhokidze, *Zhur. Obshcheĭ Khim.* (J. Gen. Chem.), **20**, 289 (1950); through *Chem. Abstracts*, **44**, 6822 (1950).

[38] W. N. Haworth, E. L. Hirst, and E. J. Miller, *J. Chem. Soc.*, **1927**, 2436; W. N. Haworth, C. W. Long, and J. H. G. Plant, *J. Chem. Soc.*, **1927**, 2809.

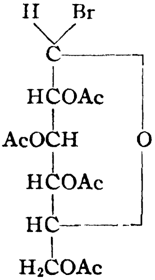
80% yield of a tetramethylgluconic acid from the right-hand side. This tetramethylgluconic acid was obviously either the 2,3,5,6- or the 2,3,4,6- variety (XI or XIII) which had previously been obtained by the oxidation, with bromine water, of the sugars corresponding to the tetramethylglucosides (VI) and (VIII), respectively. On further oxidation with nitric acid, the 2,3,4,6- acid gave the trimethoxyglutaric acid (XIV) plus the dimethoxysuccinic acid (XII) in good yield. Only the latter could be expected, or was obtained, from (XI). When dissolved in water, 2,3,5,6-tetramethylgluconic acid (XI) came into equilibrium with its lactone at the comparatively slow rate characteristic of 1,4- lactones, while the attainment of equilibrium between the 2,3,4,6- acid (XIII) and its 1,5-lactone was much more rapid.[26] 2,3,5,6-Tetramethylgluconolactone was a crystalline solid, m. p., 26–27°C., with a specific rotation of $[\alpha]_D$ 62.5° in water. The 2,3,4,6- lactone was an uncrystallized liquid with $[\alpha]_D$ 98°.



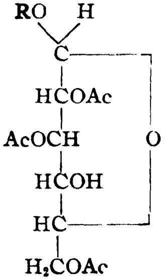
X XI XII



XIII XIV

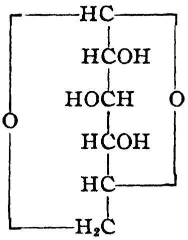


XV

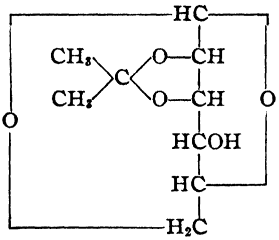


XVI

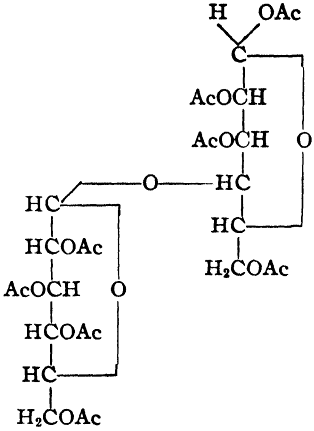
(R is CH_3 or CH_3CO)



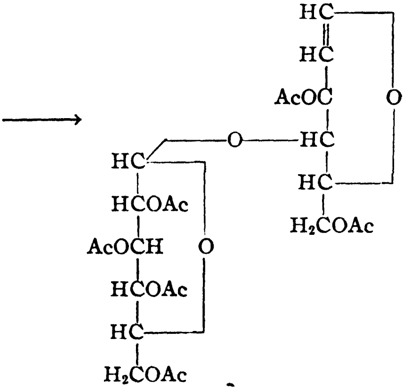
XVII



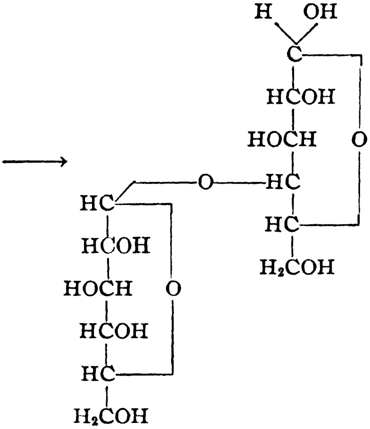
XVIII



XIX



XX



XXI

The corresponding phenylhydrazides melted at 134–36°C. and 115°C., respectively. These facts determined the structure of the two tetramethylgluconic acids and made it clear that the one actually obtained from cellobiose was the 2,3,5,6-isomer (XI).[38] The disaccharide bond in cellobiose was therefore assigned to the fourth rather than to the fifth position, and the constitution of the disaccharide was definitely proved to be 4-(β-D-glucopyranosyl)-D-glucopyranose. In accord with this structure, one mole of methyl-β-cellobioside consumed three moles of the glycol-cleaving oxidant, periodic acid, and about one mole of formic acid was produced from the unsubstituted 2,3,4-triol unit present in the molecule.[39]

Syntheses of Cellobiose. Helferich and Bredereck[40] synthesized methyl heptaacetyl-β-cellobioside by condensing "acetobromoglucose" (2,3,4,6-tetraacetyl-β-D-glucosyl bromide) (XV) with methyl 2,3,6-triacetyl-β-glucopyranoside (XVI, R is CH_3) in the presence of silver carbonate. The use, by Freudenberg and his collaborators,[41] of the corresponding methylated derivatives of glucose in the synthesis resulted in methyl heptamethyl-β-cellobioside. Freudenberg and Nagai,[42] however, were the first to synthesize cellobiose itself. They condensed "acetobromoglucose" (XV) with levoglucosan (D-glucosan <1,5>-β-<1,6>) (XVII) and obtained a mixture of partly acetylated anhydrodisaccharides in which the anhydro ring was known to be less stable toward acetolysis than the disaccharide linkage. Controlled acetolysis therefore produced some cellobiose octaacetate. Although the yields in these three syntheses were very small, the method used guaranteed that the disaccharide link in the products possessed the beta configuration and not the alpha. A much better synthetical route to cellobiose was discovered by Haskins, Hann, and Hudson[43] when they condensed "acetobromoglucose" (XV) with the 2,3-isopropylidene derivative of D-mannosan <1,5><1,6> (XVIII). The crystalline product lost the acetone (isopropylidene) residue when heated with 80% acetic acid. Mild acetolysis opened up the 1,6-anhydro ring, and crystalline 4-(β-glucopyranosyl)mannopyranose octaacetate (XIX) was obtained in an over-all yield of 20–25%. The remainder of the synthesis, leading from this acetate to the acetobromo derivative, to cellobial hexaacetate (XX), and to cellobiose (XXI),[43] had been investigated in the reverse direction by other workers.[44,45] Finally, Gilbert, Smith, and Stacey[46] dissolved an equimolecular amount of metallic sodium in very pure, molten 1,2,3,6-tetraacetyl-β-D-glucopyranose (XVI, R is CH_3CO) and obtained the 4-

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[39] T. G. Halsall, E. L. Hirst, and J. K. N. Jones, *J. Chem. Soc.*, **1947,** 1427; F. S. H. Head, *J. Textile Inst.*, **38,** T389 (1947); *Nature*, **165,** 236 (1950). The last reference pointed out that light promoted over-oxidation in this and similar cases.

[40] B. Helferich and H. Bredereck, *Ber.*, **64B,** 2411 (1931).

[41] K. Freudenberg, C. C. Andersen, Y. Go, K. Friedrich, and N. W. Richtmyer, *Ber.*, **63B,** 1961 (1930).

[42] K. Freudenberg and W. Nagai, *Ann.*, **494,** 63 (1932).

[43] W. T. Haskins, R. M. Hann, and C. S. Hudson, *J. Am. Chem. Soc.*, **63,** 1724 (1941); **64,** 1289 (1942).

[44] M. Bergmann and H. Schotte, *Ber.*, **54B,** 1564 (1921).

[45] W. N. Haworth, E. L. Hirst, H. R. L. Streight, H. A. Thomas, and J. I. Webb, *J. Chem. Soc.*, **1930,** 2636.

sodio derivative as the main product. The addition of one molar equivalent of 2,3,4,6-tetraacetyl-α-glucosyl bromide (XV) to the melt caused the separation of sodium bromide, and chromatography of the organic products recovered up to 10% of pure β-cellobiose octaacetate. It was probable that the α-acetate was also formed and that the combined yield was about 40%.

(b) CELLOTRIAOSE TO CELLOHEPTAOSE

Although the acetolysis of cotton was the favorite method of producing fractions intermediate in complexity between cellulose and cellobiose, it happened that the initial study of the above series of homogeneous, sharply defined, crystalline substances made use of an alternative method of degradation. Ordinary concentrated hydrochloric acid (38–39%) had occasionally been used to gelatinize and slowly dissolve cellulose,[47] but Willstätter and Zechmeister[48] noted that acid of about 41% concentration ($d^{15}{}_4 = 1.204$ to 1.212) gave almost immediate solution at room temperature or lower. The results with hydrobromic (66%) and hydrofluoric acid (70–75%) were similar, but cotton did not dissolve in cold, concentrated hydriodic acid. When the freshly prepared, very viscous, nonreducing solution in hydrochloric acid was kept, the viscosity rapidly diminished, an ability to reduce an alkaline copper solution became apparent, and the optical rotation, at first practically zero, increased irregularly. The last two properties finally had values close to those observed in a control experiment with glucose.

In more extensive later work, Zechmeister and Tóth[49] dissolved 400 g. of purified cellulose in 4 kg. of the 42% acid at 15°C. Three to four hours thereafter, they interrupted the reaction by removing the acid as silver chloride and evaporated the liquor to 1800 cc. Alcohol, added in successive steps to give concentrations of 60, 85, and 90%, precipitated successive fractions weighing 53 g., 25 g., and 75 g., respectively. Similar operations on the reconcentrated mother liquor precipitated a fourth fraction, 20 g., and the remainder was soluble in sufficient absolute alcohol. Each of these five fractions was refractionated from aqueous alcohol, fractions of similar optical rotatory and reducing power being combined, until at length homogeneous products were obtained. Cellobiose, 2 g., was isolated from the most-soluble fractions, which also contained glucose. Inter-

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[46] V. E. Gilbert, F. Smith, and M. Stacey, *J. Chem. Soc.*, **1946**, 622.

[47] E. Flechzig, *Z. physiol. Chem.*, **7**, 523 (1882–1883).

[48] R. Willstätter and L. Zechmeister, *Ber.*, **46B**, 2401 (1913).

[49] L. Zechmeister and G. Tóth, *Ber.*, **64B**, 854 (1931).

mediate fractions gave 2 g. of a trisaccharide, cellotriaose, and 4.8 g. of a new tetrasaccharide, cellotetraose. Finally, the least-soluble fractions deposited nonhomogeneous cellodextrins and 2 g. of a new reducing sugar which was at first thought to be a hexasaccharide and was named cellohexaose. Staudinger and Leopold[50] considered it to be cellopentaose; others doubted its homogeneity,[51] or were undecided.[52] Both these sugars, and also celloheptaose, were isolated recently by Wolfrom and his collaborators,[52] who partly acetolyzed filter paper and separated the pure α-acetates by modern chromatographic techniques. After recrystallization to constant rotation, Zechmeister and Tóth's cellotriaose and cellotetraose displayed the typical properties of mutarotating, copper-reducing aldose sugars. Their molecular weights were determined from the freezing points of their aqueous solutions, by the titration of the aldose groups with hypoiodite, and by the analyses of their crystalline phenylosazones. Pyridine and acetic anhydride gave the crystalline, fully acetylated derivatives, and deacetylation restored the original sugars. The behavior of their "cellopentaose" was similar, except that the acetate crystallized in an unsatisfactory way, and the very soluble phenylosazone was not isolated. Zechmeister and Tóth[49] also submitted cellotriaose to acetolysis and obtained cellobiose octaacetate. Cellotriaose was therefore a cellobiosylglucose, and the entire series of oligosaccharides from cellobiose to "cellopentaose" in all probability consisted of anhydroglucose units (specifically anhydro-β-glucopyranose units) uniformly linked together in an open chain for the cases $n = 2$ to $n = 5$ shown in Structure XXII (Fig. 1). This type of plane projection was introduced by Haworth[53] and gives a much more accurate idea of the probable shape and stereochemical relationship of the anhydroglucose units in these polysaccharides than the more primitive formulas hitherto used (cf. Structure VII in Section A of this Chapter III or Structure XXI).

From Formula XXII the impression might be gained that the six atoms forming the β-glucopyranose ring lie in one plane. This is certainly not so, the ring being puckered in such a manner that there is no strain on the bonds.[54] This question will be treated in detail in Chapter IV, Section B.

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[50] H. Staudinger and E. O. Leupold, *Ber.*, **67B**, 479 (1934).

[51] K. Freudenberg, K. Friedrich, and J. Bumann, *Ann.*, **494**, 41 (1932).

[52] M. L. Wolfrom and J. C. Dacons, *J. Am. Chem. Soc.*, **74**, 5331 (1952). See also E. E. Dickey and M. L. Wolfrom, *J. Am. Chem. Soc.*, **71**, 825 (1949).

[53] W. N. Haworth, *The Constitution of Sugars*, Edward Arnold, London, 1929, p. 90 and Plates I and II; see also G. V. Caesar and M. L. Cushing, *J. Phys. Chem.*, **45**, 776 (1941), especially Figs. 1–9.

[54] E. Mohr, *J. prakt. Chem.*, **98**, 315 (1918); **103**, 316 (1922).

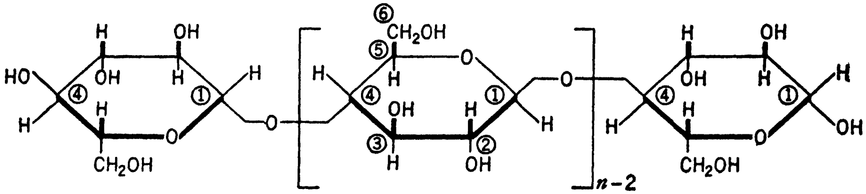

Fig. 1. (Structure XXII). Cellulose—Haworth formula.

Significant chemical features depicted are: The β-glucopyranose residue is the repeating structural unit. The units are joined through 1,4-glucosidic linkages, and the end groups differ from each other in the ring position of the carbon atom to which the terminal H and OH groups are attached. The degree of polymerization (D.P.), that is, the number of β-glucopyranose units in a cellulose chain, is equal to n; n may be odd or even.

Stereochemical relationships are emphasized by heavy and light lines in the formalized three-dimensional perspective formula. Heavy lines in the rings indicate those portions nearest the observer Heavy vertical bonds join to the ring the substituent groups which lie above the plane of the ring; light bonds, those which lie below. Thus, the completely *trans* arrangement of the ring substituents—that is, hydroxyl groups, primary alcohol groups, and glucosidic linkages—is evident. The Haworth-type formula also shows that adjacent rings are turned 180° to each other but does not show the puckered arrangement of the six atoms in the ring.

Formula XXII does however allow an excellent vizualization of the fact that the substituents around the ring, that is, two hydroxyl groups, two glucosidic linkages, and one primary alcohol group, are all *trans* to their neighbors. Molecular models, constructed with correct atomic volumes and atomic distances, strongly suggest that, when linked in the chain, the glucopyranose rings alternate in respect to the side that is uppermost. This inference, which is at once evident in Formula XXII from the alternating positions given to the primary alcoholic groups above and below the main chain, is supported by x-ray data. The models suggest that XXII can extend in a straight line and can also exist in large loops and coils, since the stereo arrangement permits of some rotation around the glucosidic bonds.

The structures of the substances corresponding to Formula XXII were checked by the methylation method for the cases $n = 3$ and $n = 4$. Haworth, Hirst, and Thomas[55] partly acetolyzed 20 g. of trimethyl cellulose, dissolved the chloroform-soluble portion of the product in acetone, and replaced acetyl by methoxyl groups by means of dimethyl sulfate and alkali. Fractional distillation at 0.1-mm. pressure then separated the fully methylated methyl glycosides of glucose, cellobiose, and cellotriaose from each other in yields of 15, 18, and 15%, respectively. Freudenberg, Friedrich, and Bumann,[51] who omitted the preliminary methylation of the cotton (100 g.) but otherwise followed a similar route, isolated the same substances in amounts of 7 g., 18 g., and 10 g., respectively. They were also successful in obtaining 5 g. of methyl hendecamethylcellotetraoside. Finally, Hess and Dziengel[56] acetolyzed cotton, deacetylated the cellotriaose fraction to the free sugar which they first purified (yield 9.9.%), and then methylated completely. All three methods of preparation gave distilled fractions from which the same series of fully methylated methyl β-glycosides crystallized. Since Haworth, Hirst, and Thomas had started from trimethyl cellulose, in which the substituents were very stable, the concordance of their results with those of the other two investigations eliminated all possibility of cellobiose or cellotriaose, or their acetates, having been formed by some reversion process or obscure rearrangement during the degradation of the cellulose. Zechmeister and Tóth[49] had earlier come to the same conclusion because glucose behaved in no abnormal way when kept in the 43% hydrochloric acid they used to degrade cellulose.

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[55] W. N. Haworth, E. L. Hirst, and H. A. Thomas, *J. Chem. Soc.*, **1931**, 824. Simultaneous deacetylation and methylation was also used by K. Freudenberg, *Ann.*, **433**, 230 (1923).

The methyl β-glycosides of decamethylcellotriaoside and hendecamethylcellotetraoside had the correct molecular weights by Rast's method and contained the correct percentages of glycosidic, as opposed to ethereal, methoxyl groups.[51] The glycosidic group was derived from the copper-reducing, right-hand end of XXII and was evolved, as methanol, when the samples were heated with a mixture of acetic and hydrochloric acids.[57] The methanol that distilled was passed through the usual apparatus and was estimated as methoxyl. When the cellotriaoside and the cellotetraoside derivatives were hydrolyzed with aqueous acid, the final rotations of the solutions were close to those calculated for a mixture of 2,3,4,6-tetramethylglucopyranose (1 mole) and 2,3,6-trimethylglucose (2 or 3 moles). The first of these scission products corresponded to that expected from the left-hand end of XXII, while the moles of the second were correct for the $n - 1$ moles of trimethylglucose derived from the $n - 2$ middle units of XXII plus the right-hand one. These fragments were actually isolated from methyl decamethyl-β-cellotriaoside in 96% and 84%, respectively, of the theoretical yields.[55] Another deduction from the Structure XXII was that the partial hydrolysis of the methylated cellotriaoside should give heptamethylcello-

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[56] K. Hess and K. Dziengel, *Ber.*, **68B**, 1594 (1935).

[57] K. Freudenberg and K. Soff, *Ann.*, **494**, 68 (1932).

TABLE 2. Physical Properties of the Cellobiose–Celloheptaose Sugars and of Cellulose[a]

Property	β-Cellobiose	α-Cellotriaose	β-Cellotetraose	β-Cellopentaose[52]	Cellohexaose[52]	Celloheptaose[52]
Formula XXII	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$
Max. yield, %[b]	40[32]	9.9[56]	1.2[49]	~1	~0.8	~0.25
Crystal form	Needles[60]	Micro-needles[49]	Micro-needles[49]	Micro-needles[49]	Cryst. powder	Cryst. powder
M. p., °C.	225[60]	206–209[c]	252–253[d]	266–268	275–278	283–286
Soly. (H_2O), %	—	25[56]	12.5[49]	4–5[49, 52]	~1	~1
$[\alpha]_D^{20\text{-}30}$ (H_2O)	(+14°) – (+34.6°)[61]	(+35°) – (+21.6°)[e,f]	(+8.4°) – (+16.5°)[e,g]	(+8°) – (+11°)[e]	+10°	+7 ± 3°
$[\alpha]_{578}^{18}$ (51% H_2SO_4)[68]	+43.3°	+32°	+25°	+13.5°	—	—
Hydrolysis const.[h]						
10^4 K at 18°	1.07	0.64	0.51–0.52	—	—	—
at 30°	6.94	4.5–4.6	3.65–3.8	3.5[52]	3.2	—
10^3 U	27.3	28.6	28.9	—	—	—
10^{16} A	3.4	18	24	—	—	—
Phenylosazone[49]						
M. p., °C. (dec.)	198	208 (uncor.)	228	—	—	—
$[\alpha]_D^{20}$ (C_2H_5OH)	−20°	−16.3°	−41°	—	—	—

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[a] Cellulose contains x-ray crystallites, decomposes without melting, is insoluble in water, and has an initial specific rotation of +2° in 51% aqueous sulfuric acid.[68] In this solvent 10^4 K at 18°C. is initially 0.304; at 30°C., 2.34[52]; 10^3 U is 29.8, and 10^{16} A, 67.[68] (See footnote *h*.)

[b] Actually isolated in pure form, cellopentaose to celloheptaose being recovered as α-acetates.

[c] Zechmeister and Tóth[49] give m. p. 238°; Hess and Dziengel,[56] m. p. 202–203°, and value quoted is from Wolfrom and Dacons.[52] These melting points depend on the mode of heating, and decomposition occurs with cellotriaose and higher members.

[d] Wolfrom and Dacons.[52] Hess and Dziengel[56] found m. p. 251°.

[e] Wolfrom and Dacons.[52] Initial rotations by logarithmic extrapolation.

[f] See also refs. 49, 56.

[g] See also ref. 49.

[h] Freudenberg and Blomqvist[68] used extrapolation to obtain these first-order constants K for the initial rate of hydrolysis in 51% sulfuric acid. The activation energies U and the steric factors A were calculated from the K values at 18° and 30°C. and the relationship $K = Ae^{-U/RT}$. The acetolysis constants of cellobiose and of cellulose were 10^4 K, 1.7 and 3.9 ± 0.3, respectively.[62]

TABLE 3. Physical Properties of the Cellobiose–Celloheptaose Acetates[a] and of Cellulose Triacetate[b] (Ref. 52 except as noted)

Property	Cellobiose	Cellotriaose	Cellotetraose	Cellopentaose	Cellohexaose	Celloheptaose
Crystal form	Small needles	Needles[63]	Micro-needles[49]	Cryst.[49,52]	Cryst.	Cryst.
M. p., °C.						
α-form	229.5[65]	223–224[c]	230–234	240–241	252–255	263–266
β-form	202[65]	209–210[49]	225[d]	—	—	—
$[\alpha]_D^{20-25}$ ($CHCl_3$).						
α-form	+41.0°[65]	+22.6°[56,e]	+13.4°	+4 2°	−0 23°	−4.4°
β-form	−15°[65]	−18.2°[56]	−15 6°[d]	−7 6°[f]	—	—
Viscosity, $[\eta]_{sp}$[g]	0.0233	0.0182	0 0164	0 0144	—	—

[a] Octa-, hendeca-, tetradeca-, heptadeca-, eicosa- and tricosa-acetate, respectively.

[b] Cellulose triacetate contains x-ray crystallites, decomposes near 295°C., has $[\alpha]_D$ ($CHCl_3$) −22.0,[64] and η_{sp} 0.0144 (see footnote g).

[c] Hess and Dziengel[56] quote m. p. 219–220°C.

[d] Zechmeister and Tóth.[49] A mixture of α and β forms.

[e] Rotational data are given for several other solvents.

[f] Zechmeister and Tóth.[49] Of doubtful identity.

[g] The specific viscosity is calculated per anhydroglucose unit in 1.4% *m*-cresol solution at 20°C.[50]

TABLE 4. Physical Properties of the Methylated Methyl β-Glycosides of the Cellobiose–Cellulose Series (Ref. 51, except as noted)

Property	Cellobiose	Cellotriaose	Cellotetraose	Cellulose
Yield, %, from cellulose	18[55]	<15[55]	<3 5	—
Crystal form	Needles	Big needles	Microneedles	X-ray micelles
B. p., °C., 0.1 mm.	160–165	215–225	260–270	>300 (dec.)
M. p., °C.	87–88	118	139	~215–216[11]
$[\alpha]_{578}$ in $CHCl_3$	−15.2°	−11.3°	− 9 8°	− 4.5° (?)
in H_2O	−16.5°	−17.0°	−16.1°	−19.1°
in CH_2OH	−16.2°	−15.5°	−15 5°	−14°
in 50% H_2SO_4[a]	− 7.5°	− 2.4°	0 3°	9.7°

[a] Extrapolation to initial rotation.

biose and 2,3,6-trimethylglucose. This was the case.[55] In a repetition of the work by Klages,[58] the cellotriaoside was heated for 90 min. at 98° in 0.4 *N* hydrochloric acid. The products isolated included some unhydrolyzed cellotriaoside, some 2,3,6-trimethylglucose, 34% of the corresponding methyl β-glucoside, and 36% of methyl heptamethyl-β-cellobioside. Further proof of the constitution of methyl decamethyl-β-cellotriaoside was provided by the synthetical work of Freudenberg and Nagai.[59] Benzyl heptamethyl-β-cellobioside was hydrogenated over palladium to toluene and the reducing sugar, which was converted to a sirupy heptamethylcellobiosyl chloride. The latter, when condensed in the presence of silver carbonate with methyl 2,3,6-trimethyl-β-glucopyranoside, gave the fully methylated derivative of methyl β-cellotriaoside. Although the yield was modest, this synthesis showed that cellotriaose was a β- rather than an α-glycoside of cellobiose and that the linkage occupied the fourth position in the reducing unit of the trisaccharide. Tables 2, 3, and 4 contain summaries of the principal physical constants observed in the cellobiose-celloheptaose series. Other physical data which have been obtained include x-ray studies of some or all of the sugars themselves, their acetates,[52,63,66] and their fully methylated methyl β-glycosides.[67]

4. Uniformity of the Glucosidic Bonds in Cellulose

(a) CHEMICAL PROOF OF STRUCTURE

The systematic application of the powerful analytical tool called the methylation method revealed the structures of the methylated derivatives of glucose, cellobiose, cellotriaose, cellotetraose, and cellulose. The first three were synthesized by methods that checked their constitution and what was known of cellopentaose in 1933 strongly suggested that it, too, fitted into the cellobiose–cellulose series. This concordant and extensive mass of

[58] F. Klages, *Ann.*, **520**, 71 (1935).

[59] K. Freudenberg and W. Nagai, *Ann.*, **494**, 63 (1932).

[60] F. C. Peterson and C. C. Spencer, *J. Am. Chem. Soc.*, **49**, 2822 (1927)

[61] C. S. Hudson and E. Yanovsky, *J. Am. Chem. Soc.*, **39**, 1013 (1917).

[62] K. Freudenberg and K. Soff, *Ber.*, **66B**, 19 (1933).

[63] G. J. Leuck and H. Mark, *J. Am. Chem. Soc.*, **56**, 1959 (1934).

[64] K. Hess and G. Schultze, *Ann.*, **455**, 81 (1927).

[65] C. S. Hudson and J. M. Johnson, *J. Am. Chem. Soc.*, **37**, 1276 (1915).

[66] L. Zechmeister and G. Tóth, *Ber.*, **68B**, 2134 (1935), discussed other x-ray data.

[67] T. Ohasi, *Bull. Chem. Soc., Japan*, **14**, 517 (1939); *Chem. Abstracts*, **34**, 2229 (1940).

research was regarded by Freudenberg as amounting to a *chemical proof* of the constitution of cellulose.[68,69]

(b) POLARIMETRIC PROOF OF STRUCTURE

As Zechmeister and Tóth[49] pointed out, the physical data in Tables 2, 3, and 4, when read from left to right, suggest that Formula XXII denoted cellulose when n was assumed to be very large. It is true that the recorded rotations of the phenylosazones (Table 2) do not alter in a regular way but this anomaly may be because osazones mutarotate. The original qualitative form of Zechmeister and Tóth's suggestion, however, by no means ruled out the possibility of variations in the chain, such as the occurrence of a few glucosidic bonds in the alpha, rather than the beta, configuration or linked to the fifth, rather than to the fourth, position in the neighboring anhydroglucose unit. Freudenberg and his collaborators[51,68] argued that, if the chain were entirely uniform, its molecular rotation would be an additive function of the rotations contributed by its individual constituent units. Since the molecular weight of cellulose was unknown, it was necessary to calculate the molecular rotations for each anhydroglucose unit before applying this deduction from the principle of optical superposition. Multiplication of the specific rotations in Tables 2, 3, and 4 by the appropriate molecular weights gave the molecular rotations, $[M]_n$, from which the molecular rotation for each glucose residue was readily obtained by dividing by the total number (n) of glucose residues in the molecule. If the left-hand end of Structure XXII had the rotation $[M]_e$, the right-hand aldehyde end $[M]_a$, and any intermediate unit $[M]_i$, then the molecular rotation of any member of the series with n units was:

$$[M]_n = [M]_e + (n - 2)[M]_i + [M]_a$$

and the rotation for each unit was·

$$\frac{[M]_n}{n} = \frac{[M]_e + [M]_a}{n} + \frac{n-2}{n}\cdot[M]_i$$

When the chain became infinitely long and n in consequence infinitely large, the latter expression reduced to $[M]_\infty/\infty = [M]_i$. In other words, the molecular rotation contributed by any intermediate unit in the chain was equal to that of an infinitely long chain, calculated for each unit. This deduction merely amounted to the statement that the rotational con

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[68] K. Freudenberg and C. Blomqvist, *Ber.*, **68B**, 2070 (1935). This article summarizes the chemical, polarimetric, kinetic, and static proofs for the constitution of cellulose.

[69] K. Freudenberg, *Tannin, Cellulose, Lignin,* J. Springer, Berlin, 1933, pp. 97–106.

TABLE 5. Molecular Rotations per Glucose Unit in the Cellobiose–Cellulose Series

Solvent	Cellobiose $\frac{M}{2}$	Cellobiose $\frac{[M]_2}{2}$	Cellotriaose $\frac{M}{3}$	Cellotriaose $\frac{[M]_3}{3}$	Cellotetraose $\frac{M}{4}$	Cellotetraose $\frac{[M]_4}{4}$ (found)	Cellotetraose $\frac{[M]_4}{4}$ (calc)	Cellopentaose $\frac{M}{5}$	Cellopentaose $\frac{[M]_5}{5}$ (found)	Cellopentaose $\frac{[M]_5}{5}$ (calc)		Cellulose $\frac{M_\infty}{\infty}$	Cellulose $\frac{[M]_\infty}{\infty}$ (found)	Cellulose $\frac{[M]_\infty}{\infty}$ (calc)		Cellulose $[\alpha]$ (found)	Cellulose $[\alpha]$ (calc)
Rotations of the Unsubstituted Sugars:							d			d	e			d	e		
Water[a]	171	+5920°	168	+3630°	166	+2740°	+2490°	165	+1820°	+1800°	+2210°	162	—	−950°	+70°	—	−2.7 ± 3°
51% H_2SO_4[b,c]	171	+7400°	168	+5400°	166	+4200°	+4400°	165	+2230°	+3800°	+3560°	162	+320°	+1400°	+1000°	2.0°	+7.4 ± 1.2°
Rotations of the Acetates in Chloroform:																	
α-Acetate	339	+13,900°	322	+7280°	314	+4210°	+3970°	308	+1290°	+1980°	+2270°	288	−6340°	−5960°	−5480°	−22.0°	−20 ± 1°
β-Acetate	339	−5090°	322	−5860°	314	—	−6250°	308	—	−6480°	—	288	—	−7410°	—	—	−25.7°
Rotations of the Methylated Methyl β-Glycosides.[b]																	
Chloroform	227	−3450°	219	−2480°	216	−2120°	−2000°	213	—	−1660°	−1850°	204	−920°	−540°	−790°	−4.5°	−3.3 ± 0.7°
Water	227	−3740°	219	−3720°	216	−3470°	−3710°	213	—	−3700°	−3420°	204	−3900°	−3680°	−3200°	−19.1°	−17.1 ± 1.2°
Methanol	227	−3680°	219	−3390°	216	−3350°	−3250°	213	—	−3160°	−3280°	204	—	−2810°	−3020°	—	−14.2 ± 0.6°
50% H_2SO_4	227	−1700°	219	−530°	216	+70°	+50°	213	—	+410°	+420°	204	+1990°	+1810°	+1840°	+9.8°	+9.0°

M = molecular weight; [α] specific rotation, [M] = M[α] = molecular rotation, n = number of glucose units in chain

[a] Equilibrium rotations

[b] Wavelength λ of light used for measuring rotations was 578 mμ, in other cases the D line of sodium, λ = 589 mμ

[c] Initial rotations.

[d] From cellobiose and cellotriaose, by equation $\frac{[M]_n}{n} = \frac{2}{n}\left(\frac{[M]_2}{2}\right) + \frac{n-2}{n}\left(\frac{M_\infty}{\infty}\right)$.

[e] From cellobiose and cellotetraose, as in Note d

tribution of the two ends of a very long chain could be neglected. The above equation therefore became:

$$\frac{[M]_n}{n} = \frac{[M]_e + [M]_a}{n} + \frac{n-2}{n} \cdot \frac{[M]_\infty}{\infty}$$

Since the experimentally observed value for cellobiose corresponded to $([M]_e + [M]_a)/2$, the following equation could be written:

$$\frac{[M]_n}{n} = \frac{2}{n}\left(\frac{[M]_2}{2}\right) + \frac{n-2}{n}\left(\frac{[M]_\infty}{\infty}\right)$$

Assuming that the observed value for cellulose was $[M]_\infty/\infty$, it was possible to calculate the molecular rotations of compounds of intermediate chain lengths such as cellotriaose ($n = 3$) or cellotetraose ($n = 4$). Conversely, the rotations of the latter made it possible to compute that of cellulose. Table 5 shows the results of such calculations.

After division by the molecular weight of an anhydroglucose unit, the calculated molecular rotations become the specific rotations of cellulose or its derivative. The value of about −2° for cellulose in water was very plausible, although the insolubility of the polysaccharide made it impossible to check this deduction directly. The concordance between the calculated values was surprisingly good in view of the fact that they were based on the rotations of the α,β-equilibrium mixtures of the reducing sugars. Perhaps the most reliable figures were obtained with the fully methylated methyl β-glycosides, which were pure, crystalline, chemical individuals. These data agreed with each other and with the observed values to within 1°, except for one chloroform and one water value, which diverged by 2° and 4°, respectively. Since the specific rotations of trimethyl cellulose and trimethyl starch differed by about 250°,[51] because starch was an α-glucosidic analog of cellulose, the alternation of one bond in every hundred from the β- to the α-glucoside configuration in the trimethyl cellulose chain would increase the rotation by about 2.5°. A systematic discrepancy of this magnitude between the observed and calculated data was not present but would have been easy to detect. Taken as a whole, the agreements were so close that Freudenberg concluded that the cellulose chain must possess the uniformity assumed in the calculation. The validity of this *polarimetric proof* of the constitution of cellulose was confirmed for cellopentaose, and extended to cellohexaose and celloheptaose, in the recent article by Wolfrom and Dacons[52] describing these sugars and their α-acetates (Tables 2 and 3).

(c) KINETIC PROOF OF STRUCTURE

If the glucosidic bonds in cellulose were equivalent, it should also be possible to account quantitatively for the course of the changes in optical rotation and in reducing power produced by acid hydrolysis. Freudenberg, Kuhn, and their collaborators set themselves this task.[68] Glucose, cellobiose, cellotriaose, and cellotetraose were separately dissolved in aqueous 51 ± 0.2% sulfuric acid, and all the solutions were 0.05 molar (9 g. per liter) in glucose when hydrolysis was complete. Duplicate solutions were kept at 18 and 30°C., and the gradual increase in the number of reducing groups was followed by means of titrations with alkaline hypoiodite solution. Optical rotations were simultaneously observed in a 2-dm. tube, and 10,000 times the observed rotation equalled the molecular rotation for each anhydroglucose unit in each case. For convenience, Freudenberg replaced the factor 10,000 by the factor 100, corresponding to an unusual definition of molecular rotation in which one gram mole was dissolved in 100 cc. of solution. The hypoiodite titration and the rotation of the glucose solutions remained practically unchanged throughout the experiment.

The titrations determined the fraction, α, of the glucosidic bonds that had undergone hydrolysis at any time, t, and the application of the first-order rate equation:

$$K = \frac{1}{t} \log \frac{1}{(1 - \alpha)},$$

gave the average value of the rate K during the first t minutes of the hydrolysis. Extrapolation to zero time then gave the initial rates K_2, K_3, K_4 reported in Table 2 for cellobiose, cellotriaose, and cellotetraose. In the case of cellobiose, the rate remained unchanged throughout the hydrolysis. With cellotriaose, a systematic variation became apparent as hydrolysis proceeded. Reference to Formula XXII ($n = 3$) makes it clear that the left-hand glucosidic bond in cellotriaose belongs to an unsubstituted glucopyranose unit, whereas the right-hand bond originates in a unit substituted in the fourth position. Since these two bonds very probably hydrolyzed at somewhat different rates, Freudenberg and Kuhn assumed that whichever one happened to break first in a given cellotriaose molecule did so at a rate equal to the average initial observed rate, K_3. Use was then made of the fact that the cleavage of either bond produced cellobiose, which then underwent scission at the uniform rate K_2. The mathematical implications of these ideas were worked out by Kuhn[70] as:

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[70] W. Kuhn, *Ber.*, **63B**, 1503 (1930), Formula 11 b. Other assumptions on the course of the degradation are also treated mathematically. The formulas are reproduced by H. Mark, *Physik und Chemie der Cellulose*, J. Springer, Berlin, 1932, pp. 293–5.

$$1 - \alpha = \frac{K_2 - K_3}{K_2 - 2K_3} e^{-2K_3 t} - \frac{K_3}{K_2 - 2K_3} e^{-K_2 t}$$

This formula[71] gave calculated values of $1 - \alpha$ that agreed excellently with those observed by the hypoiodite method throughout the entire course of the hydrolysis. The degree of hydrolysis, α, at any time, t, was also predicted correctly from the optical observations by the use of an analogous formula involving the molecular rotations of glucose, cellobiose, and cellotriaose.[68]

The hydrolysis of cellotetraose (XXII, $n = 4$) was more complicated, because here three different types of bonds were present. The two end bonds might be justifiably expected to cleave at an average rate of K_3 and, in either case, the subsequent scission of the cellotriaose unit so formed would continue along the lines already described. If the middle bond of the tetrasaccharide broke first, two molecules of cellobiose, hydrolyzing at the rate K_2, would be formed. The course of the degradation of cellotetraose obviously depended on the ratio, q, of K_3 to the rate, K_m, at which the middle bond hydrolyzed. Kuhn[70] showed that the degree of hydrolysis, α, was given by an elaborate exponential function involving q, K_2, K_3, K_4, and the time t. All these quantities were known except q and trial showed that the calculated $1 - \alpha$ versus time plot was not very sensitive to the exact value of this ratio. The calculated titration and polarimetric plots were in very satisfactory agreement with the experimental ones at 18°C., either when K_4 was taken as 0.52×10^{-4} (Table 2) and q was 1.4, or when K_4 was 0.506×10^{-4} and q was 0.8. The agreement was also satisfactory for the hydrolyses at 30°C. and the most probable value for q, both at 18 and 30°C., was considered to be 1.4 to 1.6. A similar study of the hydrolysis of cellopentaose, cellohexaose, and celloheptaose has not yet been made.

Surgical cotton, 0.05 mole of anhydroglucose units as in the other cases, was quickly dissolved in 65% sulfuric acid, and the solution was diluted to one liter of 51% acid as soon as it was possible to do so without precipitating dextrins.[68] The hydrolysis was followed optically and by hypoiodite titrations and the initial rate constant, K_n, was obtained by extrapolation from the titration data as already described. Mathematical limitations forced the use of simplifying assumptions when attempts were made to calculate the form of the rate plots. The most successful of these hypotheses was that when the long chain disintegrated, all glucosidic bonds adjacent to the reducing ends of the various-sized fragments broke at the rate K_2, and all other bonds in the fragments hydrolyzed at the rate K_n initially observed for cellulose itself. An approximate mathematical expression for $1 - \alpha$ was worked out by Klages[72] and an exact one by Kuhn[73,74] which expressed $1 - \alpha$ as an exponential function involving K_2, K_n, and t. When the calculated plots of $1 - \alpha$ against time were compared with those obtained experimentally at 18 and 30°C., both by the hypoiodite and the optical rotation methods, the agreement was within the experimental error for almost the whole course of the hydrolyses. The authors were careful to point out, however, that the mathematical assumptions underlying the work were only an approximation to the truth. For example, the calculated values of K_3 and K_4 at 18°C. were $(K_2 + K_n)/2$ and $(K_2 + 2K_n)/3$ or 0.69×10^{-4} and 0.56×10^{-4}, respectively, whereas the observed values were 0.64×10^{-4} and 0.52×10^{-4} (Table 2). An assumption still closer to reality would be that the glucosidic bonds at *both* ends of each disintegrating chain fragment were hydrolyzed at an average rate equal to K_3 and that K_n applied to all the middle links. The initial rate of hydrolysis of cellotetraose would then be $(2K_3 + K_n)/3$ or 0.515×10^{-4} at 18°C., in excellent agreement with the observed value of 0.506 to 0.520×10^{-4} (Table 2). All these rate constants were of the magnitude characteristic of glucopyranosides and the same remark was true of the corresponding activation energies. The drift in the latter from cellobiose to cellulose (Table 2), however, was possibly due to experimental error because Moelwyn-Hughes[75] reported the activation energy for the hydrolysis of cellobiose between 60 and 80°C. as 30,970, instead of Freudenberg's value of 27,300 calories.

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[71] W. Kuhn, C. Molster, and K. Freudenberg, *Ber.*, **65B**, 1179 (1932), pointed out that if the left- and right-hand bonds in triglycine (or cellotriaose) hydrolyze at rates $K\alpha$ and $K\beta$, the average observed rate K_3 is $(K\alpha + K\beta)/2$. K_1 is written for K_3 in the original article.[70]

Freudenberg and his collaborators regarded the above rate studies as a *kinetic proof* of the constitution of cellulose because the assumption was that all the hydrolyzable links in a long-chain molecule were equal and equivalent except the one at each end. This assumption was the same as that underlying the polarimetric proof. Although the results fell within the rather narrow limits of the experimental errors, the truth might be that the intermediate bonds differed very slightly according to their proximity to the end of the chain, tending to resemble those in an "infinite" chain (cellulose) when toward the middle, and grading toward those in cellobiose or cellotriaose when very close to an end.[68] The validity of these arguments was increased by the fact that $1 - \alpha$ versus time plots for the hydrolysis of cellulose could be calculated from other assumptions with results that diverged from the observed ones.[68,70] These other possibilities included the assumption that cellulose contained two types of glucosidic bonds that hydrolyzed independently at different rates; or that cellulose consisted of nonreducing, anhydrodisaccharide units that associated by means of secondary valence forces to aggregates of colloidal size.

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[72] F. Klages, *Ber.*, **65B**, 302 (1932); *Z. physik. Chem.*, **A159**, 357 (1932).

[73] K. Freudenberg and W. Kuhn, *Ber.*, **65B**, 484 (1932). K_1 is written for K_n.

[74] W. Kuhn, *Z. physik. Chem.*, **A159**, 368 (1932). K_1 is written for K_n.

[75] E. A. Moelwyn-Hughes, *Trans. Faraday Soc.*, **25**, 503 (1929); see K. Freudenberg, *Trans. Faraday Soc.*, **32**, 74 (1936).

(d) STATIC PROOF OF STRUCTURE

The polarimetric and kinetic proofs depended greatly upon extrapolation from the structures and the physical properties of the cellobiose–celloheptaose series but the degradation of cellulose gave inconsiderable yields of all these sugars except cellobiose. This serious objection to the proofs was satisfactorily overcome by considerations originating with Freudenberg[76] and later put into a mathematical form by Kuhn.[70,77] If all the glucosidic bonds in the very long cellulose chain, including those at both ends of all degraded segments, hydrolyzed at the same rate, scission would occur quite at random along the chain, and fragments of all possible intermediate lengths would soon result. As all fragments more complex than glucose were subject to further hydrolysis, the amount of one of given length, say cellotetraose, would pass through a maximum as hydrolysis proceeded. Kuhn found that for a definite degree of hydrolysis, α, the yield of the j-membered fragment was $j\alpha^2(1 - \alpha)^{j-1}$ and that the maximum yield occurred when α was $2/(j + 1)$. These relationships showed that the random breakdown of a long, uniform chain could not possibly produce more than 18.7, 13.8, 11.0, 9.1, and 7.8% of cello-triaose, -tetraose, -pentaose, -hexaose, and -heptaose, respectively. This fact completely explained the low yields of these derivatives reported in Table 2. Cellobiose octaacetate, however, was isolated by acetolysis in 42–43% of theory whereas the above calculation put the maximum possible amount at 29.8%. The difficulty was quickly traced to the fact that the ready crystallization of the substance from the acetolysis solution protected much of it from further degradation, and that in consequence the above relationships did not apply. Further calculation showed that, if cellobiose octaacetate were completely stable in the reaction mixture, no more than 66.7% would be formed. This figure made the maximum isolated yield of 42–43% entirely reasonable and completed what came to be called the *static proof* of the constitution of cellulose. The proof was not quite rigorous in the form described above because all glucosidic bonds in the chain fractions were assumed to be equivalent and the bonds at either end were known to hydrolyze rather more rapidly than the others. When allowance was made in the calculations for this factor, the maximum yields were altered by trivial percentages and the validity of the static proof was in no way impaired. In the acetolysis experiments, for example, the rate constants given in Table 3 suggested that the maximum yield of cellobiose octaacetate was 70 ± 1% instead of the 66.7% calculated by neglecting the end groups. The acetolysis rate constants were obtained as already described for aqueous hydrolysis but the final rotations of the solutions diverged substantially from each other and also from that attained by the glucose control.[62] These discrepancies were traced to the fact that acetolysis produced not only the expected mixture of 1,2,3,4,6-pentaacetyl-α- and -β-D-glucopyranose but also varying amounts of open-chain, heptaacetylgluconic aldehyde.[78]

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[76] K. Freudenberg, *Ber.*, **54B**, 767 (1921).

[77] H. Mark and A. V. Tobolsky, *Physical Chemistry of High Polymeric Systems* (High Polymers, Vol. II, 2d ed.), Interscience, New York-London, 1950, pp. 459–470.

The cumulative effect of chemical, polarimetric, kinetic, and static proofs was to answer every objection in principle to the assignment of the linear structure XXII to unaltered cotton cellulose, and decisively to refute all earlier formulas based on the physical association of small main-valence molecules. The proofs, however, assumed that the chain length of cellulose was infinite. This assumption was obviously nothing more than a mathematical convenience, and it was necessary to establish the true length of the chain by other methods. Although the agreement between experimental and calculated values in the polarimetric and kinetic proofs was close, the methods involved were not precise enough to demonstrate with certainty that 100%, rather than perhaps 99%, of the glucosidic bonds in cellulose were equivalent and of the 1,4-β-glucoside type exemplified by those in cellobiose or cellotriaose. Topic 5 below notes that these uncertainties stimulated much research during the past fifteen years, because any variation or relative chemical weakness in even 1% of these bonds would occasion variations of much greater consequence in the physical properties of cellulose.

5. Chemical Significance of Polymolecularity

(a) EARLY WORK ON THE POLYMOLECULARITY OF CELLULOSE

One of the observations that impressed the earlier investigators was the incomplete solubility of cellulose in caustic soda, and of cellulose ethers and esters in appropriate organic liquids. Not only was solution often partial but the amount dissolved varied between apparently identical samples in a capricious and unpredictable way. Conversely, when a nonsolvent was added in stages to a solution of cellulose or of a derivative, the successive fractions that were precipitated differed markedly among themselves in solubility and other physical properties but often appeared to be identical in chemical respects.[79]

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[78] K. Freudenberg and K. Soff, *Ber.*, **70B**, 264 (1937).

Berl and Klaye[80] were probably the first to note that cellulose nitrates prepared from oxidized or partly hydrolyzed cottons gave less viscous solutions than those derived from undegraded cotton. Similar observations by Ost,[81] made with cuprammonium solutions of degraded celluloses, supported Berl and Klaye's opinion that cellulose existed in many molecular sizes and that the viscosity of its solutions increased with the molecular size. When cellulose esters and ethers were fractionally precipitated with solvents, or were fractionally extracted by them, the less-soluble fractions had higher molecular weights, by osmotic pressure methods, than the more-soluble ones,[82-87] which gave lower viscosities[79,85,88,89] and sometimes passed to a limited extent through ultrafilters.[82,88] The establishment of the linear structure for cellulose made it plausible to interpret these and other results as indicating that the individual macromolecules differed in the number of glucose residues (also called anhydroglucose units or anhydro-β-glucopyranose units) they contained or in their degree of polymerization (D.P.). Cellulose, like several other colloids, is a polymolecular material and its individual macromolecules form a polymer homologous series.[90] Other terms sometimes used in the same sense are polydispersity and heterogeneity. The former is more appropriate for associated colloids like soaps than for macromolecular colloids. The latter term is suitable for systems containing two or more phases.[91,92]

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[79] J. G. McNally and A. P. Godbout, *J. Am. Chem. Soc.*, **51**, 3095 (1929).

[80] E. Berl and R. Klaye, *Z. ges. Schiess- u. Sprengstoffw.*, **2**, 381 (1907).

[81] H. Ost, *Z. angew. Chem.*, **24**, 1892 (1911).

[82] J. Duclaux and E. Wollman, *Bull. soc. chim.*, [4], **27**, 414 (1920).

[83] R. O. Herzog and A. Deripasko, *Cellulosechemie*, **13**, 25 (1932).

[84] I. Okamura, *Cellulosechemie*, **14**, 135 (1933).

[85] H. J. Rocha, *Kolloidchem. Beihefte*, **30**, 230 (1929).

[86] A. J. Medwedew, *Kunststoffe*, **23**, 249 (1933).

[87] R. O. Herzog, *Trans. Faraday Soc.*, **29**, 57 (1933).

[88] W. Kumichel, *Kolloidchem. Beihefte*, **26**, 161 (1928).

[89] I. Sakurada and M. Taniguchi, *J. Soc. Chem. Ind., Japan*, **35**, B249, B253 (1932).

[90] H. Staudinger, *Ber.*, **59B**, 3019 (1926).

[91] G. V. Schulz, *Z. Elektrochem.*, **44**, 102 (1938).

[92] H. Staudinger, *Melliand Textilber.*, **20**, 781 (1939), reviewed the origin of the concept of polymolecularity.

(b) NUMBER-AVERAGE AND WEIGHT-AVERAGE MOLECULAR WEIGHTS

Since the molecular chains in a sample of cellulose differ in length, estimations of the molecular weight or degree of polymerization give values that are merely averages. The available means of measuring molecular weights include analyses for the reducing and nonreducing end groups (see Section D of this Chapter III), the determination of viscosity as developed by Staudinger,[93,94] perfection of osmotic pressure measurements by Schulz, Svedberg, and others,[95,96] the ultracentrifuge technique of Svedberg,[97,98] together with interpretations of the streaming birefringence of cellulose solutions[99,100] and their behavior during precipitation with a nonsolvent.[101] These methods are discussed in detail in Chapter X-D; another recent survey is in the book by Hermans.[102] When the same carefully fractionated specimens are examined by any of the available methods, the results usually agree to within about 10%[103,104] but wide divergencies are frequent with the more commonly encountered, unfractionated samples. Almost simultaneous reviews of the situation by several authorities focused attention on the exact meaning of the "average" molecular weight obtained by different experimental methods with polymolecular substances.[105–107]

The classical molecular-weight determinations are derived from the laws of dilute solutions and, in effect, measure some quantity, such as the de-

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[93] H. Staudinger, *Die hochmolekularen organischen Verbindungen*, J. Springer, Berlin, 1932.

[94] H. Staudinger, *Organische Kolloidchemie*, Fr. Vieweg und Sohn, Braunschweig, 1950, p. 308.

[95] G. V. Schulz, *Z. physik. Chem.*, **A158**, 237 (1932).

[96] I. Jullander and T. Svedberg, *Nature*, **153**, 523 (1944); B. Enoksson, *J. Polymer Sci.*, **3**, 314 (1948).

[97] T. Svedberg and K. O. Pedersen, *The Ultracentrifuge*, Clarendon Press, Oxford, 1940.

[98] P. O. Kinell and B. G Rånby, in H. Mark and E. J. Verwey, editors, *Advances in Colloid Science*, Vol. III, Interscience, New York-London, 1950.

[99] W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **26**, 1394 (1943).

[100] J. J. Hermans, *Kolloid-Z.*, **106**, 22 (1944); *Rec. trav. chim.*, **63**, 25 (1944).

[101] G. V. Schulz and B. Jirgensens, *Z. physik. Chem.*, **B46**, 105 (1940); B. Jirgensens, *J. prakt. Chem.*, **161**, 30 (1942).

[102] P. H. Hermans, *Physics and Chemistry of Cellulose Fibres*, Elsevier, New York, 1949.

[103] H. Staudinger and H. Freudenberger, *Ber.*, **63B**, 2331 (1930).

[104] H. Staudinger and G. V. Schulz, *Ber.*, **68B**, 2320 (1935).

[105] W. Kern, *Ber.*, **68B**, 1439 (1935).

[106] E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 153 (1935).

[107] G. V. Schulz, *Z. physik. Chem.*, **B30**, 379 (1935). This article discusses polymolecularity originating in linear polymerizations.

pression of the freezing point, the osmotic pressure, or the elevation of the boiling point, that is proportional to the *number* of solute molecules in the quantity of substance weighed out for the experiment. Division of this weight by the number found, or by some factor proportional thereto, then gives the molecular weight, which in the case of cellulose will be very large. Division of the latter weight by the molecular weight of the repeating chemical unit of the chain (basal unit, *Grundmol*) determines the degree of polymerization. Let it be imagined that the polymer homologous mixture of different chain lengths described in the first two columns of Table 6 is prepared by weight, and is submitted to any one of these determinations. The effect produced by the first constituent will be proportional to the number of molecules, each of D.P. 200, present in 10 g. This constituent, for example, will produce an osmotic pressure proportional to 10/200. If W is the total weight in grams of any single constituent in the mixture, the combined effect produced by all the components is proportional to $\Sigma[W/\text{D.P.}]$ and the "average" degree of polymerization is $\Sigma W/\Sigma[W/\text{D.P.}]$, or 760. This kind of average is called the *number-average*. Consideration shows that if the fraction of the anhydroglucose units at one or the other end of all the cellulose chains is determined by one of the chemical end-group methods, the reciprocal of this fraction also gives the number-average degree of polymerization. A similar average would be obtained if the number of individual particles in a definite weight of a heterogeneous dust were counted under a microscope.

TABLE 6

Number-Average and Weight-Average Degrees of Polymerization

Amount, W in g	D.P.	W/D.P			$W \times$ D.P.	
10	200	10/200 or	150/3000	= 330/3000	2,000	= 32,000
20	500	20/500	120/3000		10,000	
20	1000	20/1000	60/3000		20,000	
30	2000	30/2000	45/3000	= 65/3000	60,000	= 120,000
20	3000	20/3000	20/3000		60,000	
100 g.			395/3000	= $\Sigma[W/\text{D.P.}]$	152,000	= $\Sigma[W \times \text{D.P.}]$

Number-average D.P. = 100/[395/3000] or 760.
Weight-average D.P. = 152,000/100 or 1520.

Newer methods of determining molecular weight depend not only upon the number of molecules present in a given amount of substance but also upon the *mass, size, or shape of the individual units.* Each electrically charged atom or molecule flying across the void in an Aston mass spectrograph is deflected by the transverse magnetic field to an extent determined by its individual mass and independent of the behavior of other particles.

In some cases, the observed effect for a given weight of material increases in a roughly linear fashion with particle size. For example, in light scattering the effect due to an individual particle is proportional to the square of the size of the particle,[108] but the number of particles is inversely proportional to the size. The net effect is thus proportional to the first power of the size. Similar considerations hold with viscosity, if Staudinger's law is followed (see Chapter X-D). In cases such as these, the effect produced by the first component of a mixture (Table 6) therefore tends to be proportional to g. × D.P., or to 2000, and the total effect is $\Sigma[W \times \text{D.P.}]$, leading to a weight-average degree of polymerization of $\Sigma[W \times \text{D.P.}]/\Sigma W$, or 1520. As Kraemer[109] pointed out, the weight-average D.P. can therefore be defined as the center of gravity of a weight-distribution plot.

Some methods, such as sedimentation in the ultracentrifuge, fractional solubility, and diffusion, lead to a partial separation by D.P. as well as to the evaluation of parameters such as distance traveled or fraction dissolved that depend on D.P. With this information, it is at least in theory feasible to calculate several of the possible averages, such as the number-average, weight-average, or the next higher, called the "Z" or the "C" average,[109,110] $\Sigma[W \times (\text{D.P.})^2]/\Sigma[W \times \text{D.P.}]$. The weight-average is commonly derived from equilibrium ultracentrifuge data. More involved types of average are obtained from a combination of sedimentation rate and diffusion.[111] The weight-average D.P. is of great importance in the cellulose field, because of the fact that intrinsic viscosities are closely proportional to D.P. up to a value of about 1200.[112]

The sums of the first three entries in Columns 4 and 6 of Table 6 give the contributions made in number- and weight-averages, respectively, by the less highly polymerized half of the mixture. This half is responsible for 330/3000 of the total of 395/3000 units, or for 84% of those recorded by a number-average method of estimating molecular weight. On the other hand, the same half of the sample contributes only 32,000/152,000, or 21%, of the total effect produced in a weight-average determination. Since number-average methods are heavily biased in favor of the low-molecular constituents, the degree of polymerization they register will always be less than the corresponding weight-averages when the sample is polymolecular. The discrepancy may amount to 100%, or more. Consideration of Table 6 also shows that both averages are quite independently obtained from an exact knowledge of the composition of the mixture (Columns 1 and 2) and that the one cannot be calculated from the other without this information. The determination of a number-average, therefore, does little more than set a lower limit to the possible value of the weight-average, which is often more significant.

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[108] P. Debye, *J. Applied Phys.*, **15**, 338 (1944); *J. Phys. & Colloid Chem.*, **51**, 18 (1947).

[109] W. D. Lansing and E. O. Kraemer, *J. Am. Chem. Soc.*, **57**, 1369 (1935).

[110] E. O. Kraemer, *J. Franklin Inst.*, **231**, 1 (1941); *Ind. Eng. Chem.*, **30**, 1200 (1938).

[111] I. Jullander, *J. Polymer Sci.*, **2**, 329 (1947). A review.

[112] L. Jörgensen, *Studies on the Partial Hydrolysis of Cellulose*, Emil Moestue, Oslo, 1950, pp. 48–54.

Another limitation of number-average methods is their insensitivity in the high-molecular range. Sakurada and Okamura[113] calculated that the entirely random cleavage of about 2.8 bonds per mole in a system of equally long, linear macromolecules will reduce their weight-average, and hence their intrinsic viscosity in solution, by one-half. This large effect is very easily observed. If the original substance was cellulose with a degree of polymerization 3000, as it often is in native cotton, the number of molecules in a given weight would be about 1/3000 of the number observed with glucose in similar circumstances, and the anhydroglucose unit at an end of the chain would be in a similar proportion to the whole. The scission of 2.8 bonds in 3000 would increase this fraction to about 4/3000. Both fractions are so minute that the difference between them is below the limits of accuracy of such measurements as the determination of reducing end groups by hypoiodite titration or by copper reduction, or the determination of nonreducing end groups by the tetramethylglucose or the periodate method. Very careful osmotic pressure determinations would be necessary to detect the change. Failure to recognize the unsuitability of these number-average estimations in the high-molecular field has filled the earlier literature on cellulose with erroneous claims that one treatment or another produced no degradation at all. On the other hand, weight-average methods, such as determinations of sedimentation with the ultracentrifuge or of viscosity, are sensitive toward amounts of chemical change so minute that they would otherwise pass unnoticed. The spectacular effect of atmospheric oxidation in depressing the viscosity of cellulose dissolved in cuprammonium has been emphasized for years, particularly by Staudinger,[114] who calculated that oxidation by 64 g. of oxygen may reduce the viscosity of half a ton of cotton by about 50%. On this basis, the accidental inclusion of 0.05 cc. of air in an ordinary-scale determination of viscosity in cuprammonium will have an effect of like magnitude and will ruin the estimation. When care is taken to avoid such accidents, viscosity determinations become powerful, reliable tools with which to follow chemical degradations too small to be directly measured. The aging of alkali cellulose by atmospheric oxidation, the acetolysis of cellulose during acetylation, and many other processes can readily be controlled in this way.

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[113] I. Sakurada and S. Okamura, *Z. physik. Chem.*, **A187**, 289 (1940).

A third difficulty with number-average methods lies in their marked response to the adventitious impurities frequently associated with cellulose and pulps. The small osmotic pressures developed by solutions of cellulose derivatives must be carefully distinguished from those, perhaps of comparable magnitude, that are simultaneously produced by traces of ash or other low-molecular substances. Small amounts of oxidized celluloses or other readily oxidizable impurities render the copper number, hypoiodite titration, and other determinations of reducing end groups fallaciously high, but the ease with which the carbonyl group is chemically changed may sometimes make estimations based upon it too low. Rath and Rademacher[115] illustrated this point by boiling a pulp in 0.2 to 0.5% aqueous solutions of sodium carbonate. The original copper number of 0.792 decreased by 0.290 to 0.654 unit in various experiments. Heating with sodium carbonate solutions under pressure, or with 5% caustic soda at atmospheric pressure, gave copper numbers ranging down to 0.036. Any number-average degree of polymerization that is based on the reducing end of the cellulose macromolecule is therefore very susceptible to errors introduced by the chemical pretreatment (oxidative, alkaline or otherwise) undergone by the sample.

(c) DEGREE OF POLYMOLECULARITY[102,116–118]

It is often convenient to plot the composition of the mixture described in Table 6, Columns 1 and 2, as shown in Figures 2 and 3, which are selfexplanatory. These data, however, form a highly idealized representation of polymolecularity as it exists in fact. It is extremely unlikely that any chemical process, analytic or synthetic, by which linear colloids are broken down or built up will result in a group of chain lengths, of D.P. 200 for example, to the exclusion of those at least somewhat longer or somewhat shorter. The chemical structure of the individual members of a polymer homologous series is so similar that the separation of one member from the next must depend on quantitative differences in physical properties such as solubility, which in turn are closely connected with the ratio of molecular weights. Cellotetraose was satisfactorily crystallized from its mixture with cellotriaose and cellopentaose because the difference of ±25% in the molecular weights produced sufficiently distinct solubilities. The separation of chain members of D.P. 200 from those of D.P. 199 and 201, depending on a

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[114] H. Staudinger and I. Jurisch, *Ber.*, **71B**, 2283 (1938), reviewed the earlier literature dealing with susceptibility of cellulose toward oxidation.

[115] H. Rath and H. Rademacher, *Melliand Textilber.*, **20**, 749 (1939).

[116] H. Mark and R. Raff, *High Polymeric Reactions.* (High Polymers, Vol. II), Interscience, New York-London, p. 47. See also H. Mark, *Paper Trade J.*, **113**, 34 (July 17, 1941). A more mathematical account.

[117] H. Sihtola, *Finnish Paper Timber J.*, **30**, 90, 95, 120 (1948). In Finnish, with discussion by H. Dahl and T. Bergek.

[118] A. Wannow, *Das Papier*, **5**, 75 (1951). A good general review.

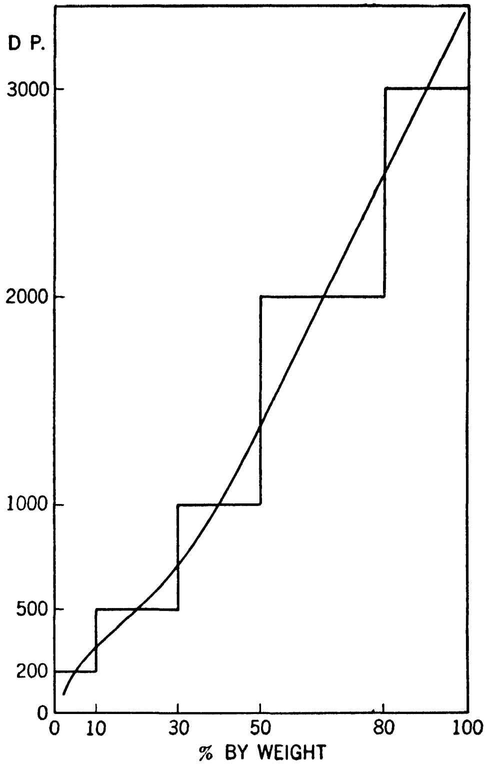

Fig 2 Integral weight distribution plot of mixture in Table 6 (page 81).

difference of ±0.5% in molecular weight, seems to be quite out of the question. From every point of view, it is justifiable to regard polymolecularity as a continuous and not as a discontinuous function, since in all but the shortest chains the discontinuities caused by a few anhydroglucose units more or less are negligible in comparison to the total chain lengths. The polymolecularity is therefore conveniently expressed by drawing the best smooth curve through the "steps" in Figure 2, or through the points in Figure 3. Differential and integral expressions can then replace the summations already described for the number- and weight-average D.P. When

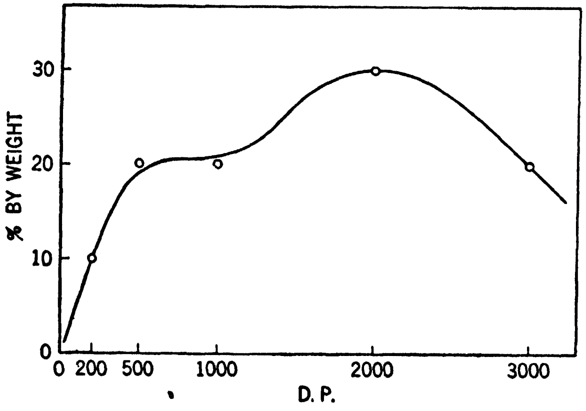

Fig. 3. Distribution plot of mixture in Table 6.

this is done, the area under the *integral weight distribution curve* (Fig. 2), given by $\int_0^{100}$ D.P. × d(%), is seen to equal 100 times the weight-average molecular weight. The first differential with respect to D.P. at each point, when plotted against the corresponding D.P., determines the *differential weight-average distribution* plot.

The determination of either the number- or the weight-average degree of polymerization is obviously insufficient to fix the shape of the plots defining the polymolecularity. A knowledge of both is also inadequate, as may be illustrated by the fact that a 59%:41% mixture of macromolecules of D.P. 500 and 3000, respectively, has practically the same number- and weight-averages as the mixture described in Table 6. Independent data are required to determine the distribution of chain lengths, even when the average degrees of polymerization are known. The problem of securing these data has been energetically studied during the past fifteen years, partly because the nature of the polymolecularity in cellulose products has an influence on their physical properties,[119-121] (see Chapter XI) and also to discover any deviations from complete uniformity in the β-glucosidic units of which the macromolecules are composed. Although Kraemer and Lansing,[106] Signer and Gross,[122] and later workers[123,124] have shown that the shape of the polymolecularity plot may be deduced from ultracentrifuge data, the method is very much more difficult with linear colloids like cellulose than with the globular proteins.[118,125,126] The most convenient procedure available is to dissolve the whole of the sample in a chemically inert solvent and to precipitate successive fractions by the stepwise addition of a nonsolvent, or by stepwise changes in temperature. Successive extractions of the original sample by liquids of increasing solvent power produce a similar fractionation which, however, is less effective.[112,127] Although further fractionation shows that the individual fractions are still nonuniform in chain length, no great error is introduced by ignoring any polymolecularity they may possess.[118] Dostal and Mark,[128] indeed, have suggested that allowance be made for this error by calculations based upon the number- and weight-averages of the individual fractions. The determination of these averages by viscosity, osmotic pressure, or other methods then makes it possible to construct a table similar to Table 6 and to plot the polymolecularity curve. Suitable solvent–nonsolvent systems[126] are

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[119] T. Kleinert and V. Mössmer, *Svensk Papperstidn.*, **51**, 541 (1948). The influence on the filterability of viscose solutions is discussed.

[120] P. C. Scherer and B. P. Rouse, *Rayon and Synthetic Textiles*, **30**, No. 11, 42; No. 12, 47 (1949); through *Chem. Abstracts*, **44**, 6118 (1950). The influence on the mechanical properties of cellulose nitrates.

[121] P. C. Scherer and R. D. McNeer, *Rayon and Synthetic Textiles*, **31**, No. 2, 53; No. 4, 54 (1950); through *Chem. Abstracts*, **44**, 7580 (1950). The influence on the mechanical properties of ethyl cellulose.

[122] R. Signer and H. Gross, *Helv. Chim. Acta*, **17**, 726 (1934).

[123] H. Mosimann, *Helv. Chim. Acta*, **26**, 61, 369 (1943).

[124] Ø. Bryde and B. G. Rånby, *Svensk Papperstidn.*, **50**, Hägglund Celebration Number, 34 (1947); *Norsk. Skogsind.*, **1**, 295 (1947); through *Chem. Abstracts*, **43**, 3195 (1949).

[125] T. Svedberg, *J. Phys. & Colloid Chem.*, **51**, 1 (1947).

[126] L. H. Cragg and H. Hammerschlag, *Chem. Revs.*, **39**, 79 (1946). A comprehensive review of methods of fractionation available in 1944.

[127] J. Jurisch, *Chem.-Ztg.*, **64**, 269 (1940).

[128] H. Dostal and H. Mark, *Trans. Faraday Soc.*, **38**, 350 (1937)

known for many cellulose nitrates,[129–135] acetates,[136] and ethers,[137] and for cellulose itself,[138,139] but it is necessary to make sure that the fractionation does not tend to separate the constituents of the sample according to their degree of chemical substitution as well as according to their D.P. Some instances of this kind have been recorded.[140,141]

The recognition that polymolecularity in varying degree was a characteristic of cellulose made it necessary to modify the early mathematical treatment of hydrolytic scission worked out by Kuhn,[70] who assumed that the initial D.P. was uniform. During the years when more general solutions to this difficult problem were being sought (see Section D of this Chapter III) a series of workers endeavored to bring greater precision into Freudenberg's kinetic proof that all the β-glucosidic bonds in cellulose were equal and uniform. Ekenstam[142] dissolved cellulose in 75% to 80% phosphoric acid as quickly as possible and attributed an initial rapid decrease in viscosity to the presence in the macromolecules of a few bonds that were hydrolyzed with unusual ease or were chemically "weak." Although the observation was confirmed by Stamm and Cohen,[142] the interpretation became unnecessary when the more appropriate number-average was substituted for the viscosity-average[143] degrees of polymerization originally

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[129] J. E. Tasman and A. J. Corey, *Pulp & Paper Mag. Can.*, **48,** No. 3, 166 (1947).

[130] H. A. Wannow and F. Thormann, *Kolloid-Z.*, **112,** 94 (1949).

[131] E. Heuser and L. Jörgensen, *Tappi*, **34,** 57 (1951).

[132] H. Haas and D. Teeves, *Makromol. Chem.*, **6,** 174 (1951).

[133] P. C. Scherer and B. P. Rouse, *Rayon Textile Monthly*, **29,** No. 8, 55; No. 9, 85 (1948); through *Chem. Abstracts*, **43,** 1965 (1949).

[134] R. L. Mitchell, *Ind. Eng. Chem.*, **38,** 843 (1946).

[135] E. Heuser, W. Shockley, and R. Kjellgren, *Tappi*, **33,** 101 (1950).

[136] P. C. Scherer and R. B. Thompson, *Rayon and Synthetic Textiles*, **31,** No. 9, 69; No. 10, 51, 54 (1950); through *Chem. Abstracts*, **45,** 8245 (1951).

[137] P. C. Scherer and R. D. McNeer, Jr., *Rayon and Synthetic Textiles*, **30,** No. 8, 56 (1949); through *Chem. Abstracts*, **43,** 8672 (1949).

[138] O. A. Battista and W. A. Sisson, *J. Am. Chem. Soc.*, **68,** 915 (1946).

[139] S. Coppick, O. A. Battista, and M. R. Lytton, *Ind. Eng. Chem.*, **42,** 2533 (1950).

[140] A. J. Rosenthal and B. B. White, *Ind. Eng. Chem.*. **44,** 2693 (1952); T. E. Timell and C. B. Purves, *Svensk Papperstidn.*, **54,** 303 (1951); F. A. Abadie, *Norsk Skogsind.*, **3,** 68 (1953). The last two articles review the literature.

[141] Constance Emery and W. E. Cohen, *Australian J. Applied Science*, **2,** No. 4, 474 (Dec. 1951).

[142] A. af Ekenstam, *Ber.*, **69B,** 549, 553 (1936); A. J. Stamm and W. E. Cohen, *J. Phys. Chem.*, **42,** 921 (1938).

[143] Bailli-Nilssen, *Tids. Kjemi Bergvesen*, **20,** 123 (1940); through *Chem. Zentr.*, **112, I,** 1811 (1941).

used in the calculation.[144] Husemann and Schulz[145] then concerned themselves with the varying relationship of the number- to the weight-average D.P. as hydrolysis proceeded. Although this relationship could be expressed as:

$$\frac{M_n}{M_w} = \frac{p}{p + 1}$$

where p was the fraction of possible chain linkages present in the sample,[146] the calculation assumed that the polymolecularity consisted of a statistical distribution of chain lengths about the mean D.P., and such a distribution could not normally be expected in a practical case. They therefore determined M_n by the osmotic method and M_w by the viscosity method, and followed the change in the nonuniformity factor U, which they defined as $(M_w/M_n) - 1$, as hydrolysis proceeded. Husemann and Schulz,[145] and also Schulz,[147] then inferred from the changes in U that a cotton of D.P. 3100 contained five regularly spaced "weak" bonds whose selective hydrolysis yielded a product containing many cellulose chains of D.P. 510 ± 5.[148–150] This concept was later extended to the degradation, by air or oxygen, of cellulose dissolved in cuprammonium or caustic soda,[151,152] although the "weak" links supposed to be regularly spaced at 600 anhydroglucose units must in these cases have been oxidized, rather than hydrolyzed, with particular ease. Other publications[117,153–156] included similar interpretations of the experimental data. The hypothesis of "weak" links in cellulose was extended by Pacsu[157] and his collaborators from presumably homogeneous hydrolyses in strong phosphoric acid[158] to heterogeneous hydrolyses in sulfuric acid,[158] 10% lactic and acetic acids,[159] and in aqueous and methanolic hydrogen chloride.[160] The results, together with those of collateral researches,[161] were considered to show that readily hydrolyzable or "weak" links occurred at regular intervals of 2^6 or 64 anhydroglucose units in the macromolecule of native cellulose, which was bound together by such links into a three-dimensional structure of high but indefinite molecular weight. Acid hydrolyses would cleave such a structure to linear molecules whose degrees of polymerization would not be determined by a random scission, but would be 64 or integral multiples thereof, according to the degree of protection against the hydrolytic agent which the physical structure of the sample afforded. Although these general concepts have been defended,[162,163] they have been severely criticized both on theoretical and experimental grounds[141,164–168] and do not seem likely to gain general acceptance.

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[144] G. V. Schulz and H. J. Löhmann, *J. prakt. Chem.*, **157**, 238 (1941).

[145] E. Husemann and G. V. Schulz, *Z. physik. Chem.*, **B52**, 1 (1942).

[146] P. J. Flory, *J. Am. Chem. Soc.*, **58**, 1877 (1936).

[147] G. V. Schulz, *Z. physik. Chem.*, **B51**, 127 (1942); *Ber.*, **80**, 335 (1947); *J. Polymer Sci.*, **3**, 365 (1948).

[148] G. V. Schulz, E. Husemann, and H. J. Löhmann, *Z. physik. Chem.*, **B52**, 23 (1942).

[149] G. V. Schulz and E. Husemann, *Z. Naturforsch.*, **1**, 268 (1946).

[150] E. Husemann and A. Carnap, *Naturwissenschaften*, **32**, 79 (1944); *Makromol. Chem.*, **1**, 158 (1947).

[151] E. Husemann and M. Goecke, *Makromol. Chem.*, **2**, 298 (1948); **4**, 194 (1949).

[152] A. Banderet and B. G. Rånby, *Helv. Chim. Acta*, **30**, 1190 (1947).

[153] E. Husemann, *Cellulosechemie*, **22**, 132 (1944); *Makromol. Chem.*, **1**, 140 (1947).

[154] A. Münster and H. Haas, *Z. Naturforsch.*, **36**, 376 (1948).

[155] T. Bergek, *Norsk Skogind.*, **2**, 289 (1948); E. J. Pagé, *Textile Research J.*, **23**, 28 (1953).

[156] T. Kleinert, G. Hingst, and I. Simmler, *Kolloid-Z.*, **108**, 137 (1944); T. Kleinert, G. Hingst, and V. Mössmer, *Kolloid-Z.*, **108**, 144 (1944); T. Kleinert and V. Mössmer, *Monatsh.*, **79**, 442 (1948); **81**, 119 (1950).

[157] E. Pacsu, *Fortschr. Chem. org. Naturstoffe*, **5**, 128 (1948). In English, an extensive discussion and review of earlier work.

By 1950, the improvement in mathematical techniques made it possible for Mark and Tobolsky[169] to recalculate much of the published viscosity data dealing with the degradation of cotton cellulose dissolved in strong phosphoric acid. These data were shown to be adequately explained from D.P. 100 to D.P. 1000 by the assumption that all the bonds hydrolyzed were of a uniform type. In the same year Jörgensen[170] published comprehensive experiments on the homogeneous and heterogeneous hydrolyses of cotton and of several wood pulps, and handled the viscosity data by advanced mathematics based on the theory of probability. This treatment, which owed much to his colleague, G. Beall, took full account of the polymolecularity of the starting material and of the varying ratio of number- to weight-averages (the relative nonuniformity) as the hydrolyses proceeded. Jörgensen came to the conclusion that the degradation of a cotton and a Mitscherlich spruce pulp followed first-order kinetics from the beginning, and that the greater initial velocity constants observed by earlier investigators (and often attributed to "weak" bonds) were not real. The hydrolyses of an aspen pulp, however, did not give any clear picture of the degradation mechanism, the indications being that "weak" links rather regular spaced at about 500 anhydroglucose units might be present. With this doubtful exception, the data were compatible with the assumption that all the glucosidic bonds in cellulose were equivalent up to a degree of polymerization of about 1300, or until the direct proportionality between the intrinsic viscosity and the first power of the molecular weight ceased to apply.

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[158] L. A. Hiller, Jr., and E. Pacsu, *Textile Research J.*, **16**, 105, 490 (1946).

[159] E. Pacsu, *Textile Research J.*, **17**, 405 (1947); *J. Polymer Sci.*, **2**, 565 (1947); P. C. Mehta and E. Pacsu, *Textile Research J.*, **18**, 387 (1948).

[160] P. C. Mehta and E. Pacsu, *Textile Research J.*, **19**, 625 (1949).

[161] P. C. Mehta and E. Pacsu, *Textile Research J.*, **19**, 699 (1949); R. Steele and E. Pacsu, *Textile Research J.*, **19**, 771, 784, 790 (1949).

[162] E. Pacsu, *Textile Research J.*, **21**, 289 (1951); G. M. Patel, *Makromol. Chem.*, **7**, 12 (1951).

[163] G. V. Schulz and I. Kömmerling, *Makromol. Chem.*, **9**, 25 (1952) re-interpret the data of Emery and Cohen (ref. 141) in favor of weak links every 465th glucose unit.

[164] K. H. Meyer, M. Studer, and A. J. A. van der Wyk, *Nature*, **164**, 786 (1949); T. G. Halsall, E. L. Hirst, and J K. N. Jones, *Nature*, **159**, 97 (1947).

[165] E. Husemann and U. Consbruch, *Makromol. Chem.*, **5**, 179 (1950); K. Matsuzaki and H. Sobue, *Bull. Chem. Soc. Japan*, **24**, 184 (1951); *J. Chem. Soc. Japan*, **54**, 289 (1951); A. Sharples, *Chem. and Ind.*, **33**, 870 (Aug. 15, 1953).

[166] A. Meller, *Tappi*, **33**, 11 (1950).

[167] R. E. Reeves, L. W. Mazzeno, Jr., and C. L. Hoffpauir, *Textile Research J.*, **21**, 78 (1951).

[168] R. E. Reeves and L. W. Mazzeno, Jr., *Textile Research J.*, **21**, 168 (1951). Also comments by Steele and Pacsu.

[169] H. Mark and A. V. Tobolsky, *Physical Chemistry of High Polymeric Systems* (High Polymers, Vol. II, 2d ed.), Interscience, New York-London, 1950, p. 469.

To sum up, the experience of recent years has almost certainly reduced the limit of error in Freudenberg's kinetic proof from perhaps 1% to perhaps 0.1% of the glucosidic bonds in cellulose. The important question as to whether or not native celluloses, with a D.P. of several thousand, contain a very few "weak" bonds, or a very few readily hydrolyzable cross bonds, does not yet seem to have received a decisive answer.

(d) SIGNIFICANCE OF THE ALKALI-SOLUBLES

It was observed at an early date that celluloses of high viscosity and high tensile strength were only slightly soluble in aqueous alkali, and that the portion dissolved contributed least to these desirable properties. According to Staudinger and Sorkin,[171] who degraded cellulose by various acid treatments, the fractions soluble in aqueous sodium hydroxide or lithium hydroxide were molecularly dispersed when the solutions were sufficiently dilute, and the intrinsic viscosities were proportional to the average degree of polymerization. This behavior, of course, was similar to that observed with solvents for undegraded cellulose, such as cuprammonium and other nitrogen-containing bases[171–173] (see Chapter X-D). Davidson[174] showed that extractions of cellulose with sodium hydroxide solutions of increasing solvent power removed fractions of increasing viscosity in cuprammonium, and he was the first to suggest that alkalies cleaved the macromolecules of oxidized cellulose at anhydroglucose units containing carbonyl groups.[175] It followed that the behavior of oxidized celluloses toward alkali was roughly the same as that of hydrocelluloses containing the same distribution of shortened molecules, and that relationships existed between the carbonyl content and the solubility in hot dilute alkali (the *alkali-stability*) of oxidized celluloses[176] and sulfite pulps.[177]

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[170] L. Jörgensen, *Studies on the Partial Hydrolysis of Cellulose*, Emil Moestue, Oslo, 1950, p. 76. G. Beall and L. Jörgensen, *Textile Research J.*, 21, 203 (1951).

[171] H. Staudinger and M. Sorkin, *Ber.*, **70B**, 1565 (1937).

Although the full extent of the decrease in tensile strength and resistance to wear of cotton textiles caused by acid degradation, and by oxidation in alkali to the nonreducing (acidic) type of oxidized celluloses, was at once revealed by direct measurement, much of the damage caused by oxidation in nonalkaline media to the reducing type of oxidized celluloses remained latent until the sample had been boiled in 1% or 2% caustic soda.[174] Unlike degradation by acids or oxidizing agents, some molds and fungi decreased tensile strength greatly without increasing the solubility in alkali[178] or the fluidity (reciprocal of viscosity) in cuprammonium[179] (see Section C-5 of this Chapter III). The great significance of the alkali-solubles to the textile industry led to the careful standardization of convenient tests, one of which was "Nodder's solubility number," or the "solubility in 10 *N* to 2 *N* caustic soda."[178,180] This test depended upon the observation of Birtwell, Clibbens, and Geake[181] that the maximum solubility of cotton in sodium hydroxide at 15° C. was attained when 10 *N* alkali was initially used and was later diluted to 2 *N*. Unmodified flax cellulose might have a solubility number of 3 or less, but chemical damage was serious when the number was 10 or 15.[178]

Perhaps the best-known test of this kind was suggested by Cross and

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[172] H. Staudinger and G. Daumiller, *Ber.*, **70B**, 2508 (1937).

[173] T. Brownsett and D. A. Clibbens, *J. Textile Inst.*, **32**, T57 (1941).

[174] G. F. Davidson, *J. Textile Inst.*, **25**, T174 (1934).

[175] G. F. Davidson, *J. Textile Inst.*, **29**, T195 (1938).

[176] A. Meller, *Tappi*, **35**, 72 (1952). The relationship was linear through the technical range of oxidation.

[177] O. Samuelson, I. Benson, and S. O. Regestadt, *Svensk Kem. Tid.*, **61**, 234 (1949); through *Chem. Abstracts*, **44**, 2234 (1950).

[178] C. R. Nodder, *J. Textile Inst.*, **22**, T416 (1931).

[179] G. O. Searle, *J. Textile Inst.*, **20**, T162 (1929).

[180] D. A. Derrett-Smith, *J. Textile Inst.*, **40**, P622 (1949).

[181] C. Birtwell, D. A. Clibbens, and A. Geake, *J. Textile Inst.*, **19**, T349 (1928).

Bevan[182] as an aid to the viscose industry, which was naturally anxious to know in advance how much of a pulp would be dissolved and lost during mercerization.[183-186] *Alpha-cellulose* was arbitrarily defined as the percentage of the sample that failed to dissolve in 17.5% caustic soda at 20° C.[186a]; neutralization of the alkaline extract precipitated *beta-cellulose;* the fraction that remained in solution was *gamma-cellulose.* The alpha-cellulose could be isolated and weighed, or the beta-cellulose and gamma-cellulose in the extract could be oxidized quantitatively with excess chromic acid,[187] the reduction of which was followed either iodometrically[188] or photometrically at a wavelength near 6000 A.[189,190] (see Chapter XII). If the sample contained hemicelluloses, ash, or residual lignin, special estimations would of course be necessary to correct for the distribution of these components among the three fractions. Ritter[191] and Launer[192] were among those who reviewed the considerable early literature dealing with the alpha-cellulose determination, and the effects of variations in technique were repeatedly studied.[183,188,193-200]

Staudinger and Feuerstein[201] estimated from viscosity measurements that gamma-cellulose included chains ranging in length up to D.P. 10, and that those in beta-cellulose increased to about D.P. 200. They therefore chose the latter figure as the minimum for alpha-cellulose. Since it was repeatedly shown[201–204] that native celluloses when degraded to an average D.P. of about 200 lost their strength, the alpha-cellulose determination appeared to have the great advantage of fractionating the sample at the D.P. range of critical importance for many purposes. At the present time it is realized that solution methods of fractionation such as this are not at all selective since many of the shorter chains are entrapped within the structure (see Chapter X-D). Even with this limitation the amount of alkali-solubles may represent the amount of highly degraded material which can contribute very little to strength. On the other hand, the alpha-cellulose estimation provided no information at all concerning the polymolecularity among the longer chains, and thus suffered in an extreme degree from the limitations inherent in a number-average determination of the degree of polymerization. In recent years, for example, Bryde[205] and Abadie[206] nitrated cotton, pulps, and even woods with a nondegrading nitric acid–phosphoric acid–phosphorus pentoxide mixture and precipitated the methanol-insoluble carbohydrate nitrates from acetone solution into much water. The precipitated fibrous cellulose trinitrate, which they called the "A-fraction," corresponded so closely in weight to that expected from the alpha-cellulose content that they regarded their procedure as a substitute for the conventional determination. Abadie and Ellefsen[207] then found that when cotton was degraded by various acid treatments to an alpha-cellulose content of 92 ± 1.2%, the viscosity D.P. of the corresponding "A-fractions" ranged from 592 to 308. When the alpha-cellulose was 65% and 50.4% the "A-fractions" had D.P.s of 178 and 190, respectively, but further degradation followed by nitration gave only more-soluble "B-fractions" of D.P. about 100 and with no cohesion. A high-grade viscose

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[182] C. F. Cross and E J. Bevan, *Researches on Cellulose (1905–1910)*, Longmans, Green & Co., London, p. 23.

[183] H. Jentgen, *Kunststoffe*, **1**, 165 (1911).

[184] Steudte, *Kunstseide u. Zellwolle*, **21**, 122 (1939); through *Chem. Abstracts*, **33**, 4429 (1939).

[185] H. Doering, *Das Papier*, **2**, 359 (1948); **3**, 37 (1949).

[186] R. Bartunek, *Das Papier*, **6**, 120 (1952).

[186a] Editor's note: It should be noted that more recent methods for alpha-cellulose determination involve dilution of the caustic to about 8% before separating the liquors from the undissolved alpha-cellulose (see Chapter XII, 2-d).

[187] C. F. Cross and E. J. Bevan, *J. Chem. Soc.*, **53**, 889 (1888).

[188] G. Porrvik, *Papier-Fabr.*, **26**, 81, 120, 133, 151, 179 (1928).

[189] C. J. Barton and A. J. Prutton, *Ind. Eng. Chem., Anal. Ed.*, **16**, 429 (1944).

[190] K. E. Ohlsson, *Svensk Papperstidn.*, **55**, 347 (1952).

[191] G. J. Ritter, *Ind. Eng. Chem., Anal. Ed.*, **1**, 52 (1929).

[192] H. F. Launer, *J. Research Natl. Bur. Standards*, **18**, 333 (1937); **20**, 87 (1938).

[193] W. Vieweg, *Papier-Fabr.*, **36**, 181 (1938).

[194] W. Ameen and B. Karlsson, *Svensk Papperstidn.*, **43**, 302, 314 (1940).

[195] H. Tydén, *Svensk Papperstidn.*, **43**, 221 (1940).

[196] L. Brissaud, *Mém. services chim. état.* (Paris), **31**, 187 (1944); through *Chem. Abstracts*, **40**, 7607 (1946).

[197] D. Johansson, *Svensk Papperstidn.*, **44**, 267 (1941).

[198] H. Doering, *Das Papier*, **2**, 359 (1948); **3**, 37 (1949).

[199] R. Bartunek, *Reyon, Synthetica, Zellwolle*, **29**, 361 (1951); through *Chem. Abstracts*, **46**, 1253 (1952).

[200] K. Wilson, E. Ringstrom, and I. Hedlund, *Svensk Papperstidn.*, **55**, 31 (1952).

[201] H. Staudinger and K. Feuerstein, *Ann.*, **526**, 72 (1936).

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[202] H. Staudinger and F. Reinecke, *Melliand Textilber.*, **20**, 109 (1939).

[203] H. Dolmetsch and F. Reinecke, *Zellwolle u. Deut. Kunstseiden-Ztg.*, **5**, 219, 299 (1939); through *Chem. Abstracts*, **34**, 1167 (1940).

[204] R. E. Dörr, *Angew. Chem.*, **53**, 13 (1940).

[205] Ø. Bryde, *Svensk Papperstidn.*, **52**, 389 (1949); Ø. Bryde and T. H. Smith, *Norsk Skogind.*, **4**, 308 (1950); through *Chem. Abstracts*, **45**, 4041 (1951).

[206] F. A. Abadie, *Compt. rend.*, **233**, 629 (1951); through *Chem. Abstracts*, **46**, 2799 (1952); *Compt. rend.*, **234**, 835 (1952).

[207] F. A. Abadie and Ö. Ellefsen, *Meddelelse fra Papirindustriens Forskningsinstitutet*, **44** (1952); *Norsk Skogind.*, **6**, 192 (1952).

[208] W. H. Algar, H. W. Giertz, and A. M. Gustafsson, *Svensk Papperstidn.*, **34**, 335 (1951); through *Chem. Abstracts*, **45**, 10576 (1951).

rayon pulp or a cotton, on the other hand, might contain 96% of alpha-cellulose with a D.P. of 1000 or more.[203]

According to recent results,[200,209] wood contained no beta-cellulose but had considerable amounts of gamma-cellulose with a D.P. of 10 to 30. Technical pulping[190,200] removed much of the latter but produced 1% or less of the former from the alpha-cellulose; bleaching with chlorite and hypochlorite left the gamma-cellulose content almost unchanged and increased the beta-cellulose somewhat, but during the aging of an alkali cellulose the beta constituent stayed constant at 0.3% while the gamma-cellulose increased from 0.7 to 2.6%. These figures were substantially increased if the alkali cellulose was washed with water and dried prior to the estimation, and increased still more if the drying was omitted.[200] Raw cotton contained only 1% of gamma-cellulose and no beta-cellulose,[210] although perhaps 1% was formed during kier-boiling in dilute alkali and in technical bleaching. Rånby,[211] who noted that the alpha- and beta-celluloses from various wood pulps resembled each other under the electron microscope and gave the same x-ray diffraction pattern, concluded that beta cellulose consisted in the main of micellar "strings" of alpha-cellulose which were still about 100 A. in diameter but were fragmented and somewhat disordered by adventitious hydrolysis or oxidation. The electron micrographs of the gamma-celluloses, however, revealed no defined structural elements and the typical x-ray diffraction pattern of cellulose was not obtained. A study of photomicrographs led Algar, Giertz, and Gustafsson[208] to make a similar distinction in type between beta- and gamma-cellulose, and they also noted a linear correlation between the amount of the latter in sundry sulfite and sulfate pulps and the accessibility toward acid hydrolysis, the increase in strength, and the decrease in opacity of the paper. Cottrall[212] had previously noted the correlation between the gamma-cellulose content and strength. Although the separation of beta- and gamma-cellulose was not quite cleancut,[190] the gamma-cellulose probably contained much more of the amorphous wood hemicelluloses such as xylan and mannan. This opinion was verified by Simmons,[213] who hydrolyzed seven pulps with acid and

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[209] H. Jentgen, *Reyon, Synthetica, Zellwolle,* **29**, No. 6, 219 (1951); R. Weller, *ibid.*, **29**, No. 7, 268 (1951); quoted from ref. 200.

[210] H. W. Giertz and G. Gran, *Svensk Papperstidn.*, **55**, 38 (1952).

[211] B. G. Rånby, *Svensk Papperstidn.*, **55**, 115 (1952).

[212] L. G. Cottrall, *Proc. Tech. Sect. Paper Makers Assoc. Gt. Britain and Ireland,* **25**, 175 (1944).

[213] J. R. Simmons, *World's Paper Trade Review,* **138**, 1766, 1768, 1770, 1771, 1772, 1777 (Dec. 4, 1952). See also J. Sundman, J. Saarnio, and C. Gustafsson, *Paper and Timber* (Finland), **33**^{4a}, 115 (1951); G. A. Adams and C. T. Bishop, *Nature,* **172**, No. 4366, 28, July 4th (1953); H. Sobue, K. Matsuzaki, A. Hatano, and Y. Arisawa, *J. Soc. Textile Cellulose Ind.* (Japan), **8**, 79 (1952); through *Chem. Abstracts,* **46**, 8851 (1952).

estimated the resulting sugars by paper partition chromatography. Several extractions with 17.5% NaOH were necessary to free the alpha-cellulose completely from xylan and mannan; the xylan and mannan in the beta-cellulose were merely occluded during the precipitation, but were the principal constituents of the gamma-cellulose.

Many authors realized that the solubility of cellulose or pulp in alkali at a single concentration and temperature was inadequate to characterize the sample, and the limited value of the alpha-cellulose determination in particular was recently reviewed with regard to rayon pulps[200,209] and filter papers.[210] Although the effect of concentration and temperature[174,188,190,193–196,200,214] is discussed in detail in Chapter X-A, it seems desirable to emphasize here that these studies led to a confusing extension of the terms beta-cellulose and gamma-cellulose to include fractions precipitated and unprecipitated, respectively, when an extract made with *any* concentration of alkali at *any* temperature was neutralized.[188] Ohlsson's suggestion[190] was that these components be described as the "beta-fraction" and the "gamma-fraction," when they were removed by sodium hydroxide of concentrations other than 17.5% or 18% at 20°C. It was observed, however, that when the concentration of caustic soda was increased from about 8% to about 16%, the amount of the "beta-fraction" recovered from technical samples by the more concentrated alkali was always very small[190,200] and the percentage of the "gamma-fraction" did not increase greatly.[195] As a first approximation, the whole of the material extracted by 17.5% or 18% NaOH at 20°C. could be called the "gamma-fraction" and was only insignificantly greater than the percentage of conventional gamma-cellulose. The maximum amount of the "beta-fraction" (and the minimum amount of the "alpha-fraction") was recovered with the concentration of caustic soda that produced the greatest swelling in the sample,[174,188,194,195,215–217] but did not depend greatly on the relative volume of the alkali, as it would if the fraction were a homogeneous chemical individual.[174] Since this maximum occurred at 20°C. near 10% caustic soda, the increase in solubility between 17.5% or 18% and 10% or 12%

[214] J. H. Ross, *Research Notes, Forest Products Laboratories of Canada*, Vol. I, 1925–27, pp. 37, 59; W. Klauditz, *Papier-Fabr.*, **38**, Tech. wiss. Tl., 213, 221 (1940); through *Chem. Abstracts*, **35**, 1225 (1941); K. Hempel, *Przeglad Papierniczy*, **5**, 62, 73, 105 (1949); quoted from ref. 190.

[215] G. F. Davidson, *J. Textile Inst.*, **27**, T112 (1936).

[216] A. Marschall, *Jentgen's Kunstseide u. Zellwolle*, **23**, 160 (1941); through *Chem. Abstracts*, **36**, 4331 (1942).

[217] O. Eisenhut, *Cellulosechemie*, **19**, 45 (1941).

alkali could be accepted as an estimate of the "beta-fraction."[188,199,200] The amount of this fraction was markedly different for native and regenerated celluloses,[217] and depended greatly on whether or not the samples had been dried[171,172] or beaten.[200,218] Moreover, the viscosity D.P. of the "beta-fractions" ranged from 65 to 530,[200,217] and the colloidal surface of the original sample appeared to be important in determining the yield.[198] These observations supported the view that the "beta-fraction" consisted of degraded cellulose with no special D.P. range or chemical character, and that its estimation afforded useful information about the reactivity and physical structure, rather than about the polymolecularity, of the sample.[186] Marschall,[219] indeed, remarked that a close relationship between the D.P. and the solubility in 10% caustic soda existed only among uniform preparations from the same cellulose.

The fact that reduction in temperature greatly increased the solubility of cellulose and pulps in alkali was used by Staudinger and his collaborators[171] to dissolve a hydrocellulose of D.P. about 470 in 2.8 *N* NaOH near 0°C., and it was possible to dissolve a regenerated cellulose of D.P. 1000 provided it had never been dried.[220] Brownsett and Davidson[221] pointed out the advantage of using 10% caustic soda at −5°C., in which undegraded cotton was almost insoluble and regenerated cellulose was almost completely soluble. The composition of mixed cotton–rayon fabrics was determined by Eisenhut[217] in particular by using this principle, and extractions with 10% caustic soda at increasing temperatures separated "beta-fractions" of decreasing chain length from which the polymolecularity of the rayon could be judged.[222] Variations of this method have been frequently applied to regenerated celluloses and rayons.[203,223,224] Extractions with sodium hydroxide, at any concentration and temperature, in the refining of wood pulps usually failed to remove xylan or mannan completely from the "alpha-fraction," perhaps because the residual 1% or 2% of these "*resistant hemicelluloses*" or "*cellulosans*"[225] were chemically combined in

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[218] A. B. Pakshver and S. S. Frolov, *J. Applied Chem.* (*U.S.S.R.*), **23**, 555 (1950).

[219] A. Marschall, *Zellwolle u. Kunstseide*, **1**, 117 (1943).

[220] H. Staudinger, *J. prakt. Chem.*, **161**, 191 (1942); H. Staudinger and J. Jurisch, *Kunstseide u. Zellwolle*, **21**, 6 (1939).

[221] T. Brownsett and G. F. Davidson, *J. Textile Inst.*, **32**, T25 (1941).

[222] R. Neumann, R. Obogi, and Z. Rogovin, *Cellulosechemie*, **17**, 87 (1936).

[223] H. Tydén, *Svensk Kem. Tid.*, **51**, 100 (1939); through *Chem. Abstracts*, **33**, 6587 (1939).

[224] S. Coppick, O. A. Battista, and M. R. Lytton, *Ind. Eng. Chem.*, **42**, 2533 (1950).

[225] L. F. Hawley and A. G. Norman, *Ind. Eng. Chem.*, **24**, 1190 (1932).

the cellulose macromolecules[226-228] (see Chapter V-B and Chapter VII).

It is evident from the preceding discussion that there is a great opportunity for confusion in the interpretation of alkali-solubility data. If three important points are kept in mind, this confusion should not be serious. The first of these points is that the various test conditions that have been suggested do not result in the extraction of all of the short-chain material. Even if equilibrium could be reached, the concentration of cellulose chains of any length would be expected to be higher in the insoluble residue than in the caustic layer, just as in any fractionation process. The second point is that equilibrium is not even closely approached in extraction processes when applied to crystalline materials such as native fibrous cellulose. Many of the shorter chains will be enclosed in the crystalline structure. As a final consideration, the alkali-soluble portions of wood pulps are largely noncellulosic in nature.

When these three sources of uncertainty are taken into account, it appears that determinations such as alpha-cellulose serve as rough guides to the loss in yield to be expected on mercerization or nitration, and also as even rougher guides to the purity of the sample. A high alpha-cellulose content however is an almost necessary criterion for a high-quality cellulose. A pulp with a high alpha-cellulose content can nevertheless be unsatisfactory in a variety of ways; for example, reactivity can be low or nonuniform, and its content of noncellulosic materials can be high.

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[226] A. Meller, *Tech. Assoc. Papers,* **30,** 214 (1947); *Paper Trade J.,* **124,** 104 (Feb. 27, 1947). This article includes an extensive literature review.

[227] L. E. Wise and E. K. Ratcliff, *Arch. Biochem.,* **19,** 292 (1948).

[228] J. G. Leech, *Tappi,* **35,** 249 (1952).

C. DEGRADATION OF CELLULOSE

1. Kinetics of Degradation Reactions

L. F. McBurney

(a) TYPES OF DEGRADATION

Cellulose, which possesses excellent strength and good stability under certain conditions, will nevertheless undergo degradation by a variety of chemical and physical processes. The most common manifestation of deterioration is a decrease in the average degree of polymerization (D.P.) of the polymer, evidenced by a loss in tensile strength of the material. This physical change is usually accompanied by a chemical modification of the cellulose molecule, such as an increase in its reducing power, or the development of reactive groups along the chain. These functional groups are generally either carboxyl or carbonyl groups or a combination of both.

Extensive degradation, for example, will frequently be brought about by exposure of cellulosic materials to the elements. This effect can be correlated in some cases with the acidity of the environment, and in such instances hydrolytic attack is a major factor. Race[1] exposed cotton yarn in Leeds, England, in each of the months of the year and measured the loss in breaking strength of the material thus exposed, as shown in Figure 4. During the winter the pH of the atmosphere and the rain was about 3, and deterioration reached a sharp peak. There was a second maximum in July, when the acidity was at a minimum, which was shown to be due primarily to photochemical oxidation. In the absence of both light and acid, loss of strength was found to be negligible.

These data serve to illustrate two of the most important types of cellulose degradation, hydrolytic and oxidative. Today, as a result of numerous investigations, it is possible to divide the types of cellulose degradation into four general classes (discussed in other subsections of this Section C of Chapter III):

1. *Hydrolytic*—cellulose is reduced in D.P. and shows an increase in reducing power.

✓2. *Oxidative*—cellulose is reduced in D.P. and the product shows a development of carboxyl and carbonyl groups.

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[1] E. Race, *J. Soc. Dyers Colourists*, 65, 56 (1949).

3. *Microbiological*—cellulose may be reduced in D.P., but loss of strength is the most pronounced effect.

4. *Mechanical*—cellulose is reduced in D.P. if the fiber is very severely treated.

From an examination of these four possible courses of cellulose deterioration the question arises as to what useful information can be derived from a detailed knowledge of the reaction kinetics involved. To answer this query it is necessary to consider each of the examples separately.

In the case of hydrolysis there are several areas of uncertainty in our knowledge. Is the reaction random in nature, or does it initiate at the ends of the chains and proceed by a systematic unzipping of the glucose units? If fiber structure is disregarded, are all the bonds comprising the chain molecule of equal strength, or are there points of inherent weakness distributed either randomly or uniformly along the chain? Can degradation be prevented or controlled so as to prepare products useful under acidic conditions? The kineticists have attempted to clarify these points by studying the reaction rates and comparing the values so obtained with those calculated from the assumptions involved in either the random theory or weak-link interpretation. The results of these studies support the random cleavage hypothesis and indicate the impossibility of preventing acid hydrolysis and the difficulties of attempting to control it so as to obtain products in a useful range of molecular weight.

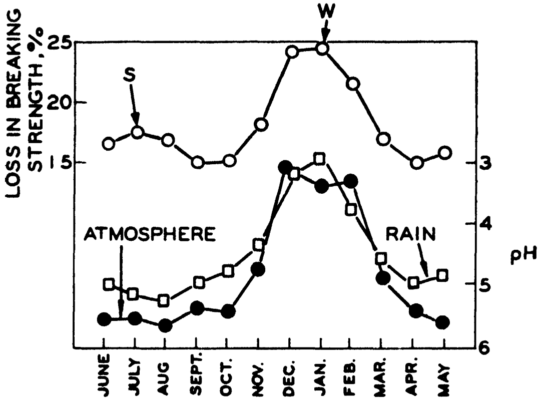


Fig. 4. Degradation of cotton yarn exposed during one year in Leeds, England (Race[1]): (S) summer peak–photooxidation; (W) winter peak–hydrolysis plus sensitized oxidation.

Oxidation of cellulose with molecular oxygen will occur readily at elevated temperature, and the reaction can be catalyzed either photochemically or by alkali. Kinetic studies in this case are of great value in establishing the nature of the process. Several questions arise; first, is the mechanism free radical or ionic; second, if free radical, what is the chain initiator; third, can the reaction be controlled or inhibited; fourth, is functional group development a direct result of the oxidation or is it a secondary effect? The answers to these questions have been obtained for only one case, that of the alkaline-catalyzed oxidation of cellulose. The mechanism in this instance has been demonstrated to be free radical in character, initiated at end groups, and subject to positive and negative catalysis.

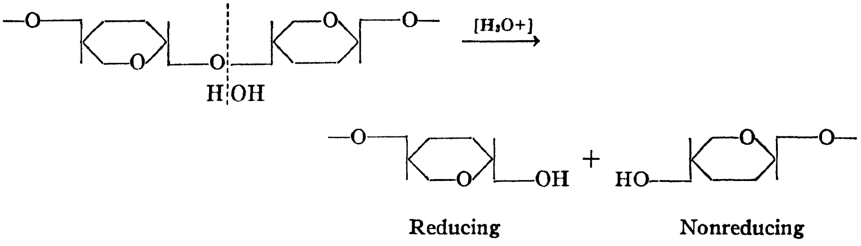
The course of microbiological and mechanical degradation has not been studied sufficiently to permit the drawing of any conclusions; thus it remains as a wide-open field for future research.

From these considerations it is apparent that a knowledge of the kinetics of cellulose reactions is of major importance. Such work will lead to the determination of the exact course of reactions and will permit application of the results to the further development of our knowledge of cellulose structure, and should develop an increased utility of cellulose as a raw material.

(b) HYDROLYSIS

The cellulose molecule, since it is bound together by acetal linkages, is extremely sensitive to acids. Acid hydrolysis, therefore, has been studied extensively, and measurements of the rate of reaction have been a distinct aid in the development of theories concerning the structure of the cellulose molecule as well as the fiber structure of the polymer.

The course of the reaction can be illustrated as follows:



Thus the addition of a water molecule to the glucosidic bond results in a chain break and an increase in the reducing power of the degraded product.

The nature of the reaction, as depicted here, would indicate the mechanism to be a case of prototropic catalysis. This stipulation has been shown to be qualitatively correct by the work of Freudenberg[2] and others. For example, Schulz and Löhmann[3] studied the rate of degradation of cotton cellulose as a function of phosphoric acid concentration under homogeneous conditions and found a linear relationship as would be predicted by the hypothesis. The first quantitative data of this type are due to Gibbons[4] who investigated the homogeneous acid hydrolysis of methyl cellulose.

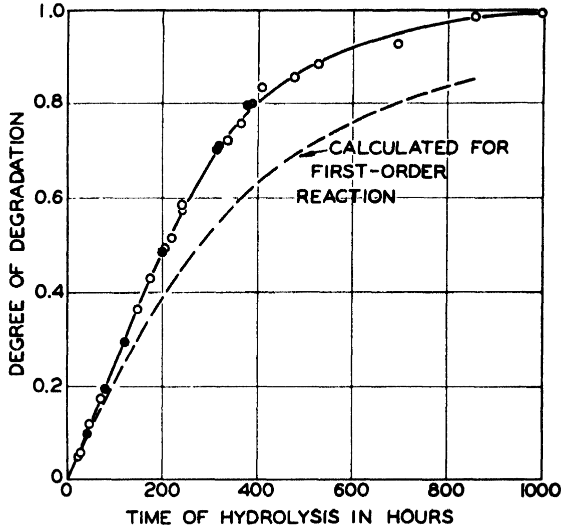


Fig. 5. The homogeneous acid hydrolysis of methyl cellulose (Gibbons[4]). Curves: (O) methyl cellulose in 1.81 *N* HCl at 50°C.; (●) cellulose in 51% H_2SO_4 at 18°C. with time scale altered by factor 0.814.

Gibbons compared the rates of degradation of cellulose in sulfuric acid and methyl cellulose in hydrochloric acid and found that they showed identical curves when multiplied by an appropriate factor (Fig. 5). Thus it would appear justified to extend the deductions, based on methyl cellulose, to cellulose itself.

The reaction appeared to follow first-order kinetics reasonably well in the range measured. The plots of rate constants against either acid concentration or activity, however, were not linear. This behavior is analogous to the results observed in the past with the hydrolysis of cane sugar. Hammett,[5] in this latter case, demonstrated that the values of log k, where k is the measured rate constant, when plotted against an experimentally determined acidity function (H_0), lie on a straight line of unit slope. The utilization of Hammett's constant is based on the assumption

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[2] K. Freudenberg and W. Kuhn, *Ber.*, **65B**, 484 (1932).

[3] G. V. Schulz and H. J. Löhmann, *J. prakt. Chem.*, **157**, 238 (1941).

[4] G. C. Gibbons, *J. Textile Inst.*, **43**, T25 (1952).

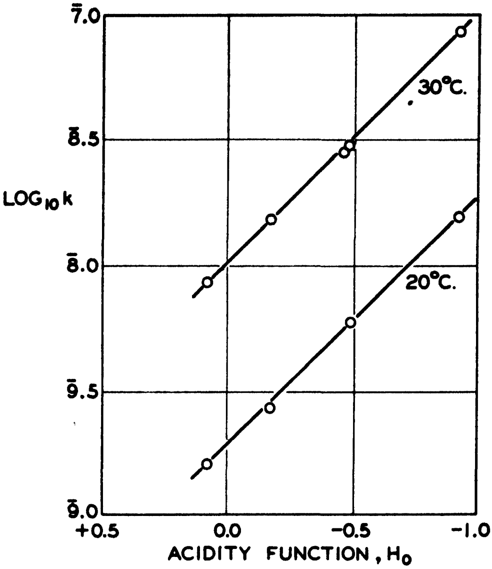

Fig 6. The homogeneous acid hydrolysis of methyl cellulose (Gibbons[4,5]).

that the reaction mechanism is of the ionization type. This can be depicted as

$$\begin{tikzcd}
S + H_3O^+ \arrow[r, shift left, "\text{fast}"] & HS^+ + H_2O \arrow[l, shift left] \arrow[d, "\text{slow}"] \\
& \text{product}
\end{tikzcd}$$

The rate of formation of the substrate ion (HS^+) is postulated as being so rapid compared to its subsequent decomposition that equilibrium exists between the ion and substrate. The rate v is then given by

$$v = k_1 C_{SH^+} = k_2 a_S a_{H_3O^+} \frac{1}{f_{SH^+}} = k_2 C_S a_{H_3O^+} \frac{f_S}{f_{SH^+}} \tag{1}$$

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[5] L. P. Hammett and M. A. Paul, *J. Am. Chem. Soc.*, **56**, 827, 830 (1934).

where f represents an activity coefficient. The ratio f_S/f_{SH^+} should be the same as that of the corresponding indicator system f_B/f_{BH^+} used to measure the acidity, and by definition

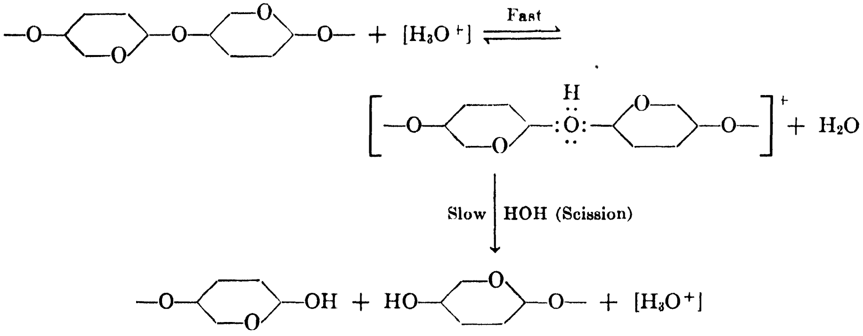
$$H_0 = -\log a_{H_3O^+}\frac{f_B}{f_{BH^+}} \qquad (2)$$

Therefore, the specific velocity constants $k = v/C_s$ will be equal to

$$\log k + H_0 = \log k_2 \qquad (3)$$

Thus a plot of log k versus H_0 should be a straight line of unit slope.

When this reasoning is applied to the hydrolysis of methyl cellulose, an excellent correspondence is found between log k and H_0 with the line showing a unit slope as is illustrated in Figure 6. Therefore it seems reasonable to suppose that the hydrolysis of both methyl cellulose and cellulose is an example of hydrogen-ion catalysis of this type, and can be illustrated by the following scheme:



The voluminous literature dealing with cellulose hydrolysis presents a rather confused picture. This is due in no small part to the fact that a majority of the investigations have dealt with a heterogeneous system of fibrous polymer undergoing reaction with aqueous acids. Under these conditions the rate of reaction is controlled by the ability of the reagents to penetrate the complex intertwined network of crystalline, mesomorphous, and amorphous regions comprising the cellulose fiber. This is in contrast to reactions of simple monomeric compounds in which all areas are assumed to be equally available for reaction, with the rate-controlling step being that of the slowest reaction. This situation is well appreciated, and the modern trend has been toward investigations in homogeneous solution where the physical effect of the fiber structure is eliminated.

(c) THEORY OF HYDROLYTIC DEGRADATION

The rate of the hydrolytic degradation of cellulose can be followed by two general techniques. The method most commonly employed is to measure the chain breaks by their effect on the solution viscosity of the polymer. The other procedure[6] is based on a measurement of the increase in the number of end groups produced by the chain scission. The two techniques differ fundamentally in that viscosity determinations are a function of the weight of the chains and depend upon the validity of Staudinger's relationship between viscosity and molecular weight for their interpretation. End-group estimation, on the other hand, gives a direct measure of the number of chains present and thus is capable of independent kinetic evaluation.

The viscosity method for measuring the heterogeneous hydrolysis of cellulose and starch was pioneered by Meyer, Hopff, and Mark.[7] The degradation of cellulose in homogeneous solution was examined by Freudenberg and coworkers.[8-12] This pioneering work established two general principles. The activation energy of the scission was shown to be approximately 28 kcal. per mole which is comparable to that of normal covalent bonds; and the rate of bond cleavage was indicated to be a function of the position of the bond relative to the ends of the cellulose molecule. The magnitude of the bond position effect is apparent by reference to Table 7.

Kuhn[9,11] made the initial attempt to predict the molecular distribution of the degraded polymer from an analysis of the reaction kinetics. This

TABLE 7

Rate of Hydrolysis of Oligosaccharides at 18°C.
(Freudenberg and Blomqvist[12])

Compound	Hydrolysis rate, min.$^{-1}$
Cellobiose	1.07×10^{-4}
Cellotriaose	0.636×10^{-4}
Cellotetraose	0.506×10^{-4}
Cellulose	0.305×10^{-4}

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[6] M. L. Wolfrom, J. C. Sowden, and E. N Lassettre, *J. Am. Chem. Soc.*, **61**, 1072 (1939).

[7] K. H. Meyer, H. Hopff, and H. Mark, *Ber.*, **62B**, 1103 (1929).

[8] K. Freudenberg, W. Kuhn, W. Dürr, F. Bolz, and G. Steinbrunn, *Ber.*, **63B**, 1510 (1930).

[9] W. Kuhn, *Ber.*, **63B**, 1503 (1930).

[10] K. Freudenberg and E. Braun, *Ann.*, **460**, 288 (1928).

[11] W. Kuhn, *Z. physik. Chem.*, **A159**, 368 (1932).

[12] K. Freudenberg and G. Blomqvist, *Ber.*, **68B**, 2070 (1935).

preliminary work has been greatly extended by Mark and Raff,[13] Simha,[14–16] Debye,[17] Jellinek,[18] Schulz,[19] Sakurada and Okamura,[20] Montroll,[21] and, most recently, by Beall and Jörgensen.[22]

These publications have been reviewed by Beall and Jörgensen and can be summarized by the statement that the complex mathematical equations derived require the use of simplifying assumptions for their solution. This has been accomplished by postulating that a random scission of the cellulose chain takes place and that chain breaks will occur with equal probability regardless of their position within the molecule. With these basic concepts, three general cases have been investigated.

I. Degradation of chains of infinite length, if all bonds split with the same probability.
II. Degradation of chains of finite uniform length, if all bonds split with the same probability.
III. Degradation of chains with finite but various lengths, if all bonds split with the same probability.

Simha[16] and Debye[17] have developed the more universal case which is:

IV. Degradation of chains of finite but various lengths, when all bonds split with different probabilities.

Although the cellulose molecule has generally been accepted to be linear in nature with the repeating anhydroglucose units (specifically anhydroglucopyranose units) joined through β-glucosidic bonds, Pacsu[23,24] in this country and Schulz and Husemann[25–27] in Germany have taken exception to this concept and have postulated the presence of "weak links" within the molecule. The nature of the structural inhomogeneities as hypothesized by these two schools is entirely different, but from kinetic considerations they would have the same influence on the hydrolytic reaction. As a result of these ideas, it is possible to distinguish two more cases, both based on the weak-link assumption.

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[13] H. Mark and R. Raff, *High Polymer Reactions* (High Polymers, Vol. III), Interscience, New York-London, 1941, pp. 221–227.

[14] E. W. Montroll and R. Simha, *J. Chem. Phys.*, **8**, 721 (1940).

[15] H. Mark and R. Simha, *Trans. Faraday Soc.*, **36**, 611 (1940).

[16] R. Simha, *J. Applied Phys.*, **12**, 569 (1941).

[17] H. Mark and R. Raff, *High Polymer Reactions* (High Polymers, Vol. III), Interscience, New York-London, 1941, pp. 226–227.

[18] H. H. G. Jellinek, *Trans. Faraday Soc.*, **40**, 266 (1944).

[19] G. V. Schulz, *Z. physik. Chem.*, **B52**, 50 (1942).

[20] I. Sakurada and S. Okamura, *Z. physik. Chem.*, **A187**, 289 (1940).

[21] E. W. Montroll, *J. Am. Chem. Soc.*, **63**, 1215 (1941).

[22] G. Beall and L. Jörgensen, *Textile Research J.*, **21**, 203 (1951).

[23] L. A. Hiller, Jr., and E. Pacsu, *Textile Research J.*, **16**, 490 (1946).

[24] E. Pacsu, *Fortschr. Chem. org. Naturstoffe*, **5**, 129 (1948).

[25] G. V. Schulz, E. Husemann, and H. J. Löhmann, *Z. physik. Chem.*, **B52**, 23 (1942).

[26] E. Husemann and A. Carnap, *Makromol. Chem.*, **1**, 140 (1947).

[27] G. V. Schulz, *J. Polymer Sci.*, **3**, 365 (1948).

V. Degradation of chains of finite uniform length, each chain containing *m* weak links distributed at random.
VI. Degradation of chains of finite uniform length, the chains having *m* weak links distributed at regular intervals.

Before a discussion of the first four mechanisms is undertaken, it is necessary to test the validity of the weak-link theories. It is obvious that if bonds of varying reactivity are present, the basic assumption of bonds all splitting with equal probability is untenable.

One theory[23,24] states that the anhydroglucose units of the cellulose chains are connected by two different types of linkages. One is the conventional 1,4-β-glucosidic bond linking the anhydroglucose units into a straight chain. The other is depicted as a 1,5-semiacetal cross-bond joining the chains in a lateral position at regular intervals, thus producing a three-dimensional structure. On this basis the hydrolysis is assumed to occur preferentially at the semiacetal bonds with the 1,4-β-glucosidic links remaining relatively unaffected by the acid. The net result of such an attack would be a rapid initial depolymerization which terminates in a "limiting D.P." represented by the size of the chains joined in the conventional fashion.

This theory was deduced from two types of experimental evidence. The application of a permanganate end-group estimation[26] to hydrolyzed cellulose gave values which were lower in reducing power than the original. This reduction was contrary to what would be expected from the classical concept of cellulose structure but could be explained by the cross-link, weak-bond assumption. Recently Husemann and Consbruch[28] have reexamined the permanganate method of end-group analysis and applied it to a variety of carbohydrates with the results shown in Table 8. It is apparent from these results that the method does not measure end groups; therefore, results based upon it are incapable of yielding any information regarding the chemical structure of cellulose.

The supporting experimental evidence employed in these studies involved the measurement of the decrease in intrinsic viscosity with hydrolysis of fibrous surgical cotton in a heterogeneous system, and the homogeneous hydrolysis of hydrocellulose dissolved in phosphoric acid. Under these conditions the decrease in rate of change of intrinsic viscosity with time was taken to indicate an approach to a limiting value of D.P.

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[28] E. Husemann and I. Consbruch, *Makromol. Chem.*, 5, 179 (1950).

TABLE 8

Titration of Mono-, Di-, and Oligo-saccharides
(Husemann and Consbruch[28])

Substance	Oxidation equivalent in milliequiv./gram	D.P By permanganate method	Actual
Glucose I	0.228	54	1
Glucose II	0.144	85	1
Glucose + ClO_2	0.105	117	1
Xylose	0.280	42	1
Maltose	0 125	100	2
Lactose	0.118	105	2
Cane sugar	0.206	60	2
Biosan	0.079	157	46

In the case of the heterogeneous hydrolysis of cellulose, the decrease in rate of cleavage is a real effect and can be ascribed to the crystalline–amorphous ratio in the fiber. Philipp, Nelson, and Ziifle[29] studied the reaction and determined the approximate velocity constants for the rate of hydrolysis of amorphous and crystalline cellulose. It can be deduced from their results that hydrolysis occurs many times faster in the amorphous region than in the crystalline. Under these conditions a rather rapid initial decrease in viscosity would occur, followed by a period of greatly reduced rate of change.

In homogeneous solution, however, the effect of fiber inhomogeneity is eliminated, and all bonds should be equally accessible to hydrolysis. Reaction rate measurement in solution, therefore, should serve to prove the presence or absence of weak links.

The rate of change of intrinsic viscosity, $[\eta]$, with time during hydrolysis does not serve as a direct measure of chain breaks. On the other hand, the reciprocal of the intrinsic viscosity, that is, intrinsic fluidity, $[\phi]$, can be related to chain breaks. When intrinsic fluidity is plotted against time under homogeneous conditions, no evidence of a decrease in rate is observed. As a result, the reaction does not appear to be approaching any limiting D.P. greater than 1.

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[29] H. J. Philipp, M. L. Nelson, and H. M. Ziifle, *Textile Research J.*, **17**, 585 (1947).

The validity of utilizing intrinsic fluidity plots can be established in the following fashion:

Assume a sample of cellulose which contains n moles of bonds per liter, capable of undergoing scission.

After hydrolysis for time t, q links will have been broken and $(n - q)$ will remain unbroken. The fraction of links remaining will then be given by $(1 - q/n)$.

Assume the rate of hydrolysis to be proportional only to the concentration of unbroken links and independent of link position. This restriction should be valid for the initial stages of the reaction. Assume also that the concentration of hydrolyzing acid is large and remains unaltered during the reaction. On this basis then, the rate of chain cleavage will be given by:

$$\frac{dq}{dt} = k\left(1 - \frac{q}{n}\right) \tag{4}$$

when $t = 0$, $q = 0$; therefore, integration of equation 4 gives

$$-\frac{1}{n}\ln\left(1 - \frac{q}{n}\right) = kt \tag{5}$$

Expanding the left-hand side of the equation in a series gives:

$$-\ln\left(1 - \frac{q}{n}\right) = \frac{q}{n} + \frac{1}{2}\left(\frac{q}{n}\right)^2 + \frac{1}{3}\left(\frac{q}{n}\right)^3 + \dots \frac{1}{i}\left(\frac{q}{n}\right)^i \tag{6}$$

When n is large in comparison to q, as is the case in the early stages of hydrolysis, the higher members of the series can be disregarded so that

$$-\ln\left(1 - \frac{q}{n}\right) \longrightarrow \frac{q}{n} \tag{7}$$

Substituting (7) in (5) yields

$$\frac{q}{n} = nkt \tag{8}$$

or

$$q = k't \tag{9}$$

Thus for the early stages of reaction the rate of chain breaking is a simple zero-order reaction with respect to time.

For a given weight of polymer W, the number of chain breaks q is equal to the increase in the number of molecules, thus:

$$q = N_s - N_0 = \Delta N = \Delta\left(\frac{W}{M_n}\right) \tag{10}$$

where N_s is the number of molecules present after scission, N_0 is the number of molecules initially present, and M_n is the number-average molecular weight. For a randomly degraded polymer, the number-average molecular weight is approximately one half the weight-average molecular weight as pointed out by Flory.[30] The weight-average molecular weight is given by

$$\bar{M}_w = \frac{\sum\limits_{i=0}^{\infty} M_i^2 n_i}{\sum\limits_{i=0}^{\infty} M_i n_i} = \frac{\sum\limits_{i=0}^{\infty} M_i W_i}{\sum\limits_{i=0}^{\infty} W_i} \tag{11}$$

and the viscosity-average molecular weight by

$$\bar{M}_\eta = \left[\frac{\sum\limits_{i=0}^{\infty} M_i^{\alpha+1} n_i}{\sum\limits_{i=0}^{\infty} M_i n_i}\right]^{1/\alpha} \tag{12}$$

where M_i and n_i are the molecular weight and number of molecules, respectively, of species i.

When the constant α in the formula for viscosity-average molecular weight equals unity, $\bar{M}_w = \bar{M}_\eta$; in those cases where α deviates from unity, $\bar{M}_w$ and $\bar{M}_\eta$ are not too different. This can best be demonstrated by a simple example. Take a hypothetical polymer mixture composed of equal quantities (1 g.) of material of different molecular weights; i.e., 100 and 200, and 5 g. of a third substance of molecular weight 500. Assign to α the arbitrary value of 0.5. On this basis, $\bar{M}_w$ will be 400, and $\bar{M}_\eta$ will be 373. These values vary by only 6%. Cellulose and cellulose derivatives have values of α which deviate but little from the ideal case of $\alpha = 1$, so that the error observed by using the relation

$$\bar{M}_w = k[\eta] \tag{13}$$

will be much less than 6%.

On this basis, the following expression can be established:

$$q = \Delta\left(\frac{W}{M_n}\right) = \Delta\left(\frac{2W}{K[\eta]}\right) \tag{14}$$

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[30] P. J. Flory, *J. Am. Chem. Soc.*, **58**, 1877 (1936).

By definition

$$[\phi] = 1/[\eta] \tag{15}$$

where $[\phi]$ = intrinsic fluidity.
Therefore:

$$q = \Delta\left(\frac{2W\,[\phi]}{K}\right) \tag{16}$$

Collecting the constants gives

$$\frac{2W}{K} = K' \tag{17}$$

$$q = K'\Delta[\phi] \tag{18}$$

Substituting equation 18 in equation 9:

$$K'\Delta[\phi] = k't \tag{19}$$

$$\Delta[\phi] = \left(\frac{k'}{K'}\right)t \tag{20}$$

From equation 20 it is obvious that a plot of intrinsic fluidity change versus time would be linear for that portion of the hydrolysis reaction which corresponds to the boundary assumptions involved in the derivation. In addition, the slope of the curve would be a measure of the rate at which depolymerization is occurring. If a limiting D.P. is being approached, however, the rate of the reaction should decrease and approach zero.

In normal practice it is not necessary to utilize the intrinsic fluidity change since a simple intrinsic fluidity plot will yield a curve of the same slope but transposed in the direction of the ordinate so that it no longer passes through the origin.

In Figure 7, the data of Hiller and Pacsu[23] on hydrolysis of hydrocellulose and surgical cotton in phosphoric acid solutions have been replotted in the form suggested by equation 20; the required linearity is observed for the first 50 hrs. of hydrolysis. Following this initial rate of reaction, an acceleration in rate is observed and not a decrease as would be the case if a limit were being approached. In fact no evidence of any retardation in velocity is observed over the entire course of the reaction as measured, even though the final intrinsic viscosity is far below the limiting value postulated from work on fibrous hydrolysis.

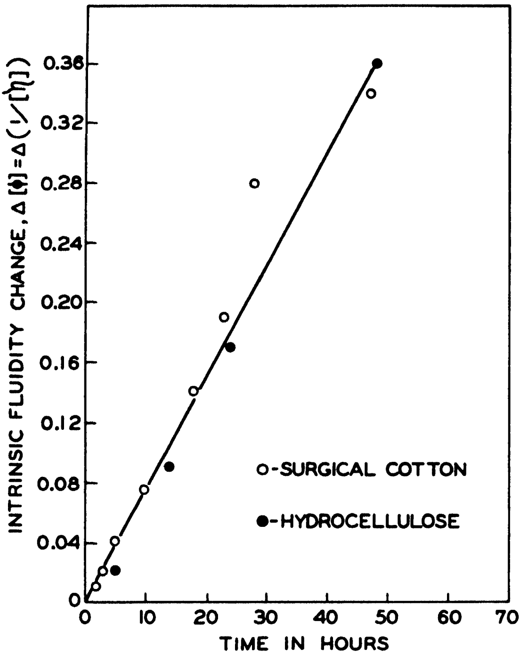

Fig. 7. Hydrolysis of cellulose in H_3PO_4 solution at 20°C. Data of Hiller and Pacsu[23] (see Fig. 8) replotted in the intrinsic fluidity form.

For comparison, the same data are plotted in the original intrinsic viscosity form in Figure 8. These curves fail to give any indication of the rate at which chains are being broken and lead to the misconception that the reaction is slowing down. Nor is it possible to deduce the fact that the samples of both surgical cotton and hydrocellulose are degrading at the same rate over the period of measurement. When these data are converted to the intrinsic fluidity form, it is immediately apparent that no decrease in rate is occurring and that the chains are being broken with identical rates in both the surgical cotton and hydrocellulose. This illustration gives an excellent example of the utility of intrinsic fluidity plots when a kinetic interpretation of the data is desired.

The discontinuity in the reaction after 50 hrs. can be attributed to three factors:

1. The molecular size was reduced to the extent that it is no longer correct to neglect the higher terms of equation 7.

2. The change in rate of bond cleavage is due to the end-group effect as noted by Freudenberg.[8]

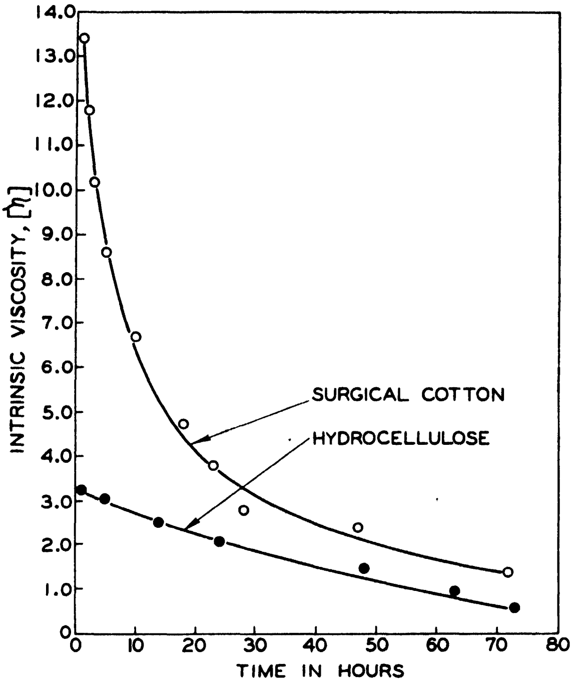

Fig. 8. Hydrolysis of cellulose in H_3PO_4 solution at 20°C. Data as plotted by Hiller and Pacsu.[23]

3. The linear relationship between D.P. and [η] is valid only in the intermediate range of D.P.

Martin[31] also investigated the solution hydrolysis of cellulose with both 67% sulfuric acid and 39% hydrochloric acid as solvents at 0°C. He interpreted his results on the basis of intrinsic fluidity plots and showed that the simple linear relationship adequately describes the results over the entire range of measurement which extended above and below the so-called limiting value of D.P. The work of Sihtola[32] on the hydrolysis of cellulose in zinc chloride solution at 80°C. and the work of Ekenstam[33] on phosphoric acid solutions of filter paper at 20°C. yield similar results when plotted in the same fashion (Fig. 9).

From the experimental evidence described, viscosity studies fail to establish the presence of any weak links in the cellulose chains within the measured D.P. limits. The criticism of the classical cellulose structure therefore must be regarded as unfounded.

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[31] A. F. Martin, Am. Chem. Soc. meeting, Boston, April 1-5, 1951.

[32] H. Sihtola, *Die Hydrolyse der Cellulose*, Helsinki, 1944.

[33] A. af Ekenstam, *Cellulose-Lösungen in Mineralsäuren*, Bloms, Lund, 1936.

Schulz, Husemann, and coworkers[25–27] have advanced their theory of "langperiodische Struktur des Cellulosemolekules" which states that the cellulose molecule is built up of uniform β-glucosidic chains containing different groups at regular intervals of 500 units. The exact nature of the weak links has not been definitely identified by these workers, but they have been ascribed tentatively to the presence of xylose units in the chain. Comparative hydrolysis rate measurements of xylan and cellulose indicated the former to react 1500 times more rapidly than cellulose, and thus xylose units would be a point of preferential attack or weak links.

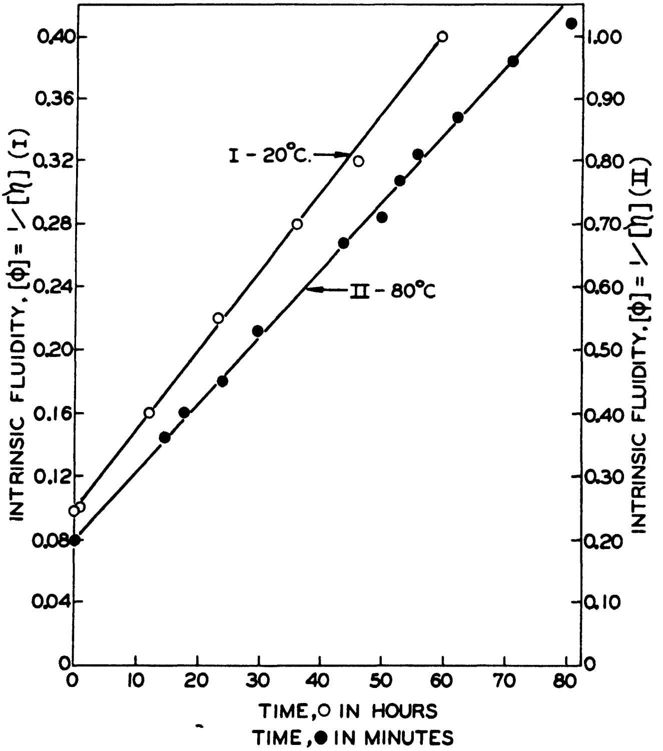

Fig. 9. Hydrolysis of cellulose: data of Sihtola[32] in $ZnCl_2$ solution at 80°C.; data of Ekenstam[33] in H_3PO_4 solution at 20°C.

These conclusions were based initially on the evaluation of kinetic and frequency-distribution data from both heterogeneous and homogeneous hydrolysis of cellulose and later from similar work on ramie cellulose. These data, when obtained from measurement of heterogeneous systems, are subject to the same criticism as was applied to Pacsu's work. The results can be explained equally well on the basis of the fiber structure of cellulose. The reaction will occur rapidly in the amorphous region and much more slowly in the crystalline region; consequently, a decrease in over-all hydrolysis rate would be expected as the amorphous region is destroyed.

In examining the homogeneous hydrolysis of cellulose in the light of the weak-link theory, Schulz reasoned that weak links will be broken preferentially during hydrolysis; thus, as the D.P. is reduced, the degradation constant will also show a reduction.

Utilizing the same reasoning that was employed previously in developing equation 7, and taking into account the higher terms in the expansion, Schulz developed the following expression:

$$k = 1/t \ln \frac{\left(1 - \frac{1}{\bar{P}_a}\right)}{\left(1 - \frac{1}{\bar{P}_t}\right)} \tag{21}$$

where $\bar{P}_a$ = initial D.P. and $\bar{P}_t$ = mean D.P. at time t. The constant k, therefore, should be independent of D.P. if all the bonds in the polymer have the same hydrolysis constant. If hydrolysis is not random and/or weak links are present, then k will be dependent upon D.P.

Schulz and Löhmann[3] tested this equation by studying the rate of hydrolysis of phosphoric acid solutions of cellulose; their results are illustrated in Table 9. From these data it would be assumed that the rate of hydrolysis is independent of D.P. between 1530 and 100 and that there is no evidence of any weak links. In a later publication, however, Schulz and Husemann[34] discounted the results obtained from the two samples

TABLE 9

Degradation of Cotton Cellulose in 13.1 M H_3PO_4 at 29°C.
(Schulz and Löhmann[3])

Average D.P.	1530	1010	482	383	174	131	60	32	19.5
$k \times 10^6$ min.$^{-1}$	6.08	6.48	6.52	6.63	6.61	6.66	8.37	9.99	23.5

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[34] E. Husemann and G. V. Schulz, *Z. physik. Chem.*, **B52**, 1 (1942).

of highest D.P. on the basis that the samples were not uniform, and thus the results could not be relied upon. They did conclude, though, that no weak links existed below a D.P. of 500.

More recently, Jörgensen[35] conducted some exhaustive studies on the rate of homogeneous hydrolysis of cellulose in phosphoric acid, and determined the rate constant on the basis of both weight-average and number-average molecular weights as shown in Table 10. It is apparent from these results that when the hydrolysis constant is calculated from number-average D.P.'s, it remains uniform over the range of 1250 to 100. When the change in relative nonuniformity during hydrolysis is taken into consideration, data are obtained which indicate that homogeneous cellulose degradation occurs as a first-order cleavage of the interunit bonds from the beginning, with no evidence of weak links in the molecule.

TABLE 10

Hydrolysis of Cotton Cellulose Samples in H_3PO_4 Solution at 25°C. (Jörgensen[35])

Sample	Time of hydrolysis, hrs.	Average D.P.		Hydrolysis constants × 10^3	
		$D.P._w$	$D.P._n$	k_w	k_n
1	0	1600	1245	—	—
2	15	1410	1080	5.6	8.2
3	60	1055	785	5.3	7.8
4	135	760	530	4.9	8.1
5	210	612	410	4.2	7.4
6	330	468	300	4.2	7.4
7	750	258	152	4.1	7.7
8	1140	182	104	4.1	7.8
9	2100	101	54	4.6	9.3

To summarize the status of the weak-link theory, it can be said that no evidence has been obtained for such inhomogeneities in cellulose by measurements of hydrolysis rates in homogeneous solutions. It must be emphasized that these conclusions are based to a large extent on work done in phosphoric acid where cellulose of high D.P. is insoluble; there is even some question of the solubility of well-crystallized samples of low D.P. (see Chapter X-A). In the case of heterogeneous hydrolysis, a distinct decrease in the rate of reaction is observed and can be explained by the accepted fiber structure of the polymer. The rate of hydrolysis of the amorphous region has been shown to be greater than that of the crystalline region, and since the ordered area of cellulose is much greater than the disordered, the hydrolysis rate will be high initially and show a rather rapid decrease with time as the amorphous region disappears. Consequently, there is no need for the elaboration of Cases V and VI based on the weak-link assumption.

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[35] L. Jörgensen, *Studies on the Partial Hydrolysis of Cellulose*, Emil Moestue, Oslo, 1950.

The discussion will therefore now be directed toward the first four general cases, which have been utilized to predict the molecular distribution of a degraded polymer from an analysis of the reaction kinetics. The assumptions involved in Case I will be examined first.

The hypothesis which differentiates Case I from Cases II and III is the assignment of infinite length to the undegraded polymer. This is admittedly an oversimplification of the true situation since cellulose, as we deal with it, has a finite length which is a function of the method utilized in its isolation and purification. It is fortunate for most approximations that cellulose behaves as though it had been randomly degraded from infinite length so that this concept is of value. Predictions of molecular-weight distribution on further degradation, based on this hypothesis, do not agree with those determined experimentally so a complete discussion of the theory will not be given.

The results of considering depolymerization as a random process occurring with molecules whose initial size is uniform and of finite length (Case II) has received considerable attention in the literature.[13,14,17] In general, the frequency of occurrence of a molecule of size j resulting from the degradation of a larger molecule is given by:

$$F_j = \sum_{\lambda=j+1}^{\infty} pq^j(\lambda p - jp - p + 2)\phi_\lambda \tag{22}$$

and the probability of F_j occurring without degradation is

$$F_j = q^j\phi_\lambda \qquad (j = \lambda) \tag{23}$$

where λ is the initial size of the molecule, j is size of the molecule resulting from degradation, p is the chance of a bond being broken, $q = 1 - p$ is the chance of a bond surviving, and ϕ_λ is the frequency of occurrence of a molecule of size λ relative to the frequency of occurrence of all the molecules in the initial polymer.

Examination of equations 22 and 23 makes it apparent that their solution is dependent upon the ability to assign a functional form to ϕ_λ, which represents the initial polymer distribution. In case II this has been accomplished by assuming all the molecules to be of a uniform size and thus eliminating ϕ_λ from consideration. It was pointed out previously that the cellulose utilized in most investigations is a material whose mean average size has resulted through a random degradation from its native state. It is not reasonable to assume that the nature of the initial degradation will differ from that in the isolated condition; therefore, the polymer cannot be perfectly uniform unless it has been fractionated to separate it into its component parts. Calculations based on equations 22 and 23 and on the assumption of Case II will apply exactly, then, to ideally uniform fractions of the polymer and only inexactly to cellulose as normally studied.

In Case III the molecular size of the initial polymer has been considered to be nonuniform. This avoids the restrictions of Cases I and II, and should be of considerable interest, since it would be expected to apply generally under conditions of homogeneous hydrolysis.

Montroll[21] examined this possibility, but in order to deal with the mathematical form of the equation it was necessary to assume the initial distribution to be normal or Gaussian in character. Even with this simplification, the expression for mean weight-average degree of polymerization is highly complicated. Such conditions probably apply reasonably well to cotton cellulose, and in this instance Montroll's treatment should be applicable. In wood pulps, however, the distribution is quite abnormal, with the materials showing two or more maxima in the frequency distribution curves. Under these conditions his equation could not be expected to apply, and the mathematical solution of the general Case IV would be rendered prohibitively complex.

Beall and Jörgensen[22] in reviewing this work have attributed the failure to devise a general practical method for predicting the frequency distribution to attempts to relate the partially degraded distribution (F_L) to that of the initial polymer ϕ_λ. This distribution can be determined experimentally, but in most cases it will not be characterizable by any known mathematical function. This eliminates the possibility of assigning a realistic form to ϕ_λ in equations 22 and 23 and necessitates the assumptions utilized and discussed in Cases I, II, and III.

The degradation of chains with finite but nonuniform length when all bonds break with different probabilities (Case IV) has been examined by Simha[16] and Debye.[17] This is the most general and all-inclusive possibility examined to date, and has the further advantage of involving no assumptions regarding the nature of the initial distribution or the mechanism of bond cleavage. As would be anticipated from the previous considerations, the mathematical form for solution of this case is much too general and complicated to be applied to any specific system.

Beall and Jörgensen have recently examined this problem and developed an approach which appears to avoid the difficulties encountered in the previous work. They have made use of Montroll's idea of representing a nonnormal distribution as the sum of a series of distributions. Their approach differs, however, in that they relate the statistical moments of distribution of the degraded polymer to the corresponding moments of the initial material, thus avoiding the assignment of a functional form to the distribution frequency of the original polymer. The "moments" are an estimate of corresponding parameters of theoretical distributions to which the moments would usually tend if the sample were increased indefinitely. The physical significance of the moments can be better appreciated by pointing out that they are involved in the general estimate of molecular weight of polymolecular materials. The first three moments are proportional to the number-average, weight-average, and "Z"-average molecular weights.

On this basis it is possible to define the moments of the initial distribution as

$$\mu_r = \frac{\sum_{\lambda=0}^{\infty} \lambda_r \phi_\lambda}{\sum_{\lambda=0}^{\infty} \phi_\lambda} = \sum_{\lambda=0}^{\infty} \lambda^r \phi_\lambda \tag{24}$$

where $r = 1,2,3,4 \ldots$
and

$$\sum_{\lambda=0}^{\infty} \phi_\lambda = 1$$

λ	is the number of links in a molecule of the initial cellulose of size λ.
ϕ_λ	is the frequency of initial molecules of size λ.
L	is the number of links in a molecule of degraded cellulose of size L.
F_L	is the frequency of degraded molecules of size L.
P	is the chance of a link being broken.
$q = (1 - p)$	is the chance of a link surviving.

The moments of the degraded distribution m_r will be given by

$$m_r = \frac{\sum_{L=0}^{\infty} L^r F_L}{\sum_{L=0}^{\infty} F_L} \tag{25}$$

where

$$\sum_{L=0}^{\infty} F_L \neq 1$$

The first three moments (r = 1, 2, and 3) are available from the molecular weights as pointed out previously so that:

$$
\begin{aligned}
\overline{\text{D.P.}_n} &= \frac{\bar{M}_n}{m} = \frac{\sum_{\lambda=0}^{\infty} \lambda\phi_\lambda}{\sum_{\lambda=0}^{\infty} \phi_\lambda} = \mu_1 \\
\overline{\text{D.P.}_w} &= \frac{\bar{M}_w}{m} = \frac{\sum_{\lambda=0}^{\infty} \lambda^2\phi_\lambda}{\sum_{\lambda=0}^{\infty} \lambda\phi_\lambda} = \frac{\mu_2}{\mu_1} \\
\overline{\text{D.P.}_z} &= \frac{\bar{M}_z}{m} = \frac{\sum_{\lambda=0}^{\infty} \lambda^3\phi_\lambda}{\sum_{\lambda=0}^{\infty} \lambda^2\phi_\lambda} = \frac{\mu_3}{\mu_2}
\end{aligned}
\tag{26}
$$

Obviously, the more r is extended, the better is the definition of the distribution. From these considerations it is apparent that m_r will be dependent upon μ_r in the same manner as F_L is dependent upon ϕ_λ. By the use of moments, it is possible to consider the initial and resultant distributions without reference to their exact form. It is possible then to estimate m_r and to check these estimates against those determined experimentally. If agreement between these values of m_r for various r's is obtained, the original hypothesis is sustained.

By the use of sufficient moments it is possible to characterize fully any distribution. These calculations will become increasingly involved as the number of moments is increased, particularly in cases where more than one maximum is involved. With cotton, which has but one mode, the distribution curve can be determined with relatively few moments and for this reason it was chosen for testing the theory.

In Figure 10A a comparison is made between the number-frequency distribution of a cotton cellulose sample determined experimentally and that constructed from the found moments. In Figure 10B the actually determined frequency curve is compared with that obtained from the calculated moments. In both cases the agreement obtained can be considered excellent. Figure 10B also shows the calculated distribution curve when the assumption of a uniform starting material (Case II) is made. In this latter instance there is no agreement between the calculated and the experimentally determined results. This comparison is an excellent example of the lack of agreement obtained in the past when attempts were made to predict distribution curves on the basis of the simplifying assumptions discussed under Cases I and II.

Figures 10C and 10D illustrate the result obtained with another sample of cotton cellulose on the same basis as discussed for Figures 10A and 10B. In this case, correspondence is not so close but is still much better than would have been obtainable under previous assumptions. Exact correlation would not be anticipated since no perfect fractionation procedure has been developed. Experimentally determined frequency curves therefore are subject to considerable variation. Another source of uncertainty lies in the method of developing the distribution curves from the moments based on Pearson's system.[36,37] This is a statistical procedure for charac-

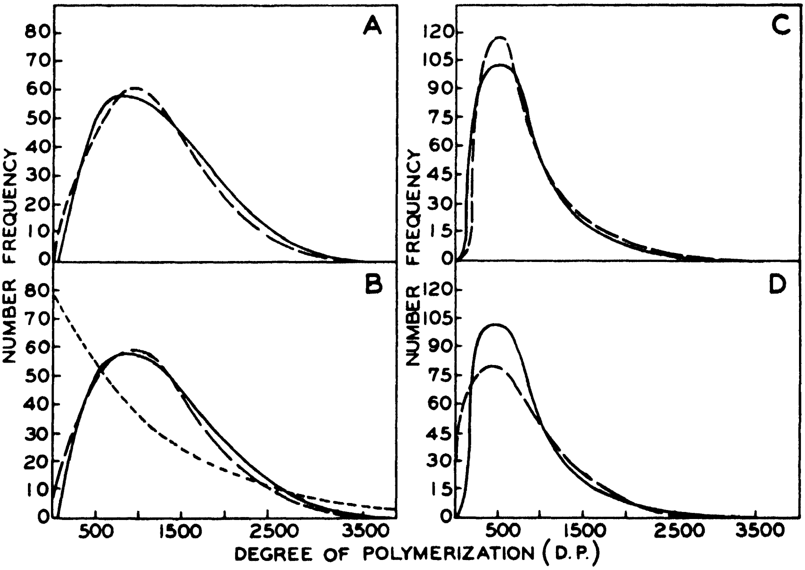

Fig. 10. Frequency distribution of cotton cellulose according to Beall and Jörgensen.[22] Curves in (A) and (B) represent data on one sample; those in (C) and (D) on another. Solid lines are actually determined distribution curves; broken lines are those calculated from found moments. The dotted curve in (B) is calculated under the assumption of a uniform starting material.

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[36] W. P. Elderton, *Frequency Curves and Correlation*, 3d ed., University Press, Cambridge, 1938, pp. 38–127.

[37] M. G. Kendall, *The Advanced Theory of Statistics*, Vol. I, 2d ed., Griffin and Co., London, 1945, pp. 137–150.

terizing distributions with one mode and which approach the abscissa smoothly. The results obtained in Figures 10C and 10D seem to indicate that the curves might have been in better agreement had a different Pearson distribution type been chosen.

The method of statistical moments thus appears to be the most practical tool developed for estimating the nature of the frequency distribution of a degraded polymer. To utilize this procedure for an unequivocal proof of the theory of random hydrolysis would require the calculation of many more than the first three moments. This would necessitate an enormous amount of work and would hardly be justified. It does appear, however, to give strong evidence in favor of random hydrolysis.

The present status of the kinetics of homogeneous hydrolysis can be summarized as follows:

1. Cellulose hydrolysis is an example of prototropic catalysis.
2. The rate of cellulose hydrolysis can be measured conveniently by intrinsic fluidity change.
3. The kinetics can be adequately described, within the intermediate molecular weight range, as zero order with respect to time.
4. The preponderance of evidence supports the assumption that hydrolysis is a random process with no evidence of periodic weak links in the cellulose molecule.
5. A method has been developed by which the frequency distribution of the degraded polymer can be estimated from a knowledge of reaction rate and number-average, weight-average, and "Z"-average molecular weights.

(d) HETEROGENEOUS HYDROLYSIS

Fibrous or heterogeneous hydrolysis of cellulose, from a technical viewpoint, is of far greater importance than is its homogeneous counterpart. The majority of cellulose reactions occur with cellulose as a separate insoluble phase. Thus a thorough knowledge of the reaction kinetics would be of great value. The theoretical and practical difficulties implicit in investigations of the kinetics of heterogeneous hydrolysis are such that very little is known about the mechanism involved. The majority of the investigators have been satisfied to deduce empirical equations which express their experimental observations and, as a result, have not attempted any theoretical development of the reaction kinetics. These studies, for the most part, have dealt with kinetics only incidentally as a means of evaluating relative crystalline-to-amorphous ratios in the fiber. The conclusions based on this work will be discussed in detail in Chapter IV-B.

Experimental methods which have been used to measure fibrous hydrolysis and their kinetic interpretations can be summarized as follows: End-group estimation based on copper number was employed by Birtwell, Clibbens, and Geake,[38] and their results were expressed as

$$\text{Copper number} = ct^n \tag{27}$$

where t is the time of hydrolysis and c and n are constants. This equation was found to be valid only in the early stages of reaction and is therefore of limited value. A similar expression was advanced by Yorston[39] from weight-loss measurements during hydrolysis:

$$x = ct^n \tag{28}$$

where x equals the percentage loss in weight at time t, with c and n as constants. This relationship also proved to have a limited applicability.

Nickerson[40] and Conrad and Scroggie[41] utilized a different experimental approach and followed the reaction by measuring carbon dioxide evolution, in the presence of ferric chloride, during acid hydrolysis. They interpreted the hydrolysis–time plots as a composite of a zero-order reaction superimposed upon a fast reaction. A similar technique was utilized by Lovell and Goldschmid[42] to explain results obtained from weight-loss measurements.

Philipp, Nelson, and Ziifle[29] and Nelson and Conrad[43] employed the loss-in-weight method and took into account the humic substances formed from the glucose produced during hydrolysis. They formulated their results as concurrent first-order reactions with the crystalline and amorphous components, and showed the total unhydrolyzed cellulose R at time t to be given by

$$R = c_0 e^{-k_c t} + a_0 e^{-k_a t} \tag{29}$$

where

c_0 = initial concentration of crystalline cellulose.
a_0 = initial concentration of amorphous cellulose.
k_c = rate of hydrolysis of crystalline cellulose.
k_a = rate of hydrolysis of amorphous cellulose.

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[38] C. Birtwell, D. A. Clibbens, and A. Geake, *J. Textile Inst.*, **17**, 1457 (1926).

[39] F. H. Yorston, *Quart. Rev.*, Forest Products Laboratory of Canada, No. 13, 16 (1933).

[40] R. F. Nickerson, *Ind. Eng. Chem.*, **33**, 1022 (1941); **34**, 85, 1840 (1942).

[41] C. C. Conrad and A. G. Scroggie, *Ind. Eng. Chem.*, **37**, 592 (1945).

[42] E. L. Lovell and O. Goldschmid, *Ind. Eng. Chem.*, **38**, 811 (1946).

[43] M. L. Nelson and C. M. Conrad, *Textile Research J.*, **18**, 149 (1948).

Meller[44] also used the weight-loss technique and resolved the rate plots by extrapolating the linear portions of the curve to the ordinate and drawing a parallel line through the origin. This procedure was justified since the rate plots were reasonably straight lines for almost the entire range of measurement. Thus the rate-controlling step is depicted as zero order with respect to time and is ascribed to the difficultly accessible portion of the cellulose fiber. His results permitted calculation of the activation energy which was found to be 28–29 kcal. per mole.

It is apparent from this brief review that a considerable divergency of opinion exists as to the actual kinetics involved in the fibrous hydrolysis of cellulose. As a first approximation it would appear most likely that the reaction would be dependent upon the number of available bonds in the accessible and less accessible regions. This would require the kinetics to be first order with respect to time. This approximation appears to be true for the accessible regions of the fiber but does not explain the zero-order behavior found by Meller. Examination of his data reveals that the reactions were not carried beyond a maximum of 20% weight loss and the majority of his studies showed a maximum of only 5 to 10%. It is possible that at this low level of degradation the rate would approximate a zero-order character as was shown to be applicable for solution hydrolysis.

Another possibility exists; namely, the bonds in the less accessible region are not equally available to the acid so that the rate-controlling step is not the scission of the bonds but rather the rate of diffusion of acid to the glucosidic linkages. In this case the reaction would appear to be zero order since it is diffusion controlled. The high activation energies found militate against this possibility since the majority of diffusionary processes have activation energies below 15 kcal. per mole.

(e) OXIDATION

Cellulose, in common with other hydroxy compounds, can be oxidized by a variety of reagents. The degree of degradation which accompanies this reaction depends both on the nature of the oxidizing reagent and the conditions employed.

The periodate ion, for example, converts the hydroxyls in the 2 and 3 positions into aldehyde groups but does not directly bring about chain breaks. Chain degradation, however, will occur if the dialdehyde is subjected to alkaline reagents. Thus by the proper choice of reagent, functional groups can be introduced into the molecule with either retention or loss of the original molecular size. Molecular oxygen, on the other hand, is nonspecific in its action and will bring about the introduction of functional groups and a simultaneous chain scission.

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[44] A. Meller, *J. Polymer Sci.*, **4**, 619 (1949).

From a commercial viewpoint the autoxidation of cellulose by molecular oxygen in the presence of alkali is of major importance as well as being a recognized chemical phenomenon. The rapid depolymerization of cellulose in cuprammonium solution, for example, has necessitated elaborate precaution in the utilization of this medium for the determination of cellulose viscosities. Schulz[45] has investigated the reaction and found the rate of depolymerization to be proportional to the square root of the oxygen pressure.

Consideration of the alkaline oxidation reaction of cellulose, in light of present-day knowledge of autocatalysis, leads to the conclusion that it is probably a chain reaction with free-radical propagation. This complex reaction is further complicated by the physical nature of the cellulose since the oxidation most commonly encountered is the heterogeneous one between molecular oxygen and alkali cellulose. For such a mechanism to be operative under these conditions, a very considerable chain mobility must be assumed in the alkali cellulose.

The necessity for mobility of chains can be appreciated by consideration of a typical reaction mechanism, in this case, that of a hydrocarbon.[46–48]

$$\begin{aligned}
&\mathrm{R{-}H} + \mathrm{O_2} &&\xrightarrow{\text{slow}} \mathrm{R\cdot} + \mathrm{\cdot HO_2}\\
&\mathrm{R\cdot} + \mathrm{O_2} &&\xrightarrow{\text{fast}} \mathrm{ROO\cdot}\\
&\mathrm{ROO\cdot} + \mathrm{RH} &&\xrightarrow{\text{fast}} \mathrm{ROOH} + \mathrm{R\cdot}\\
&\mathrm{ROOH} &&\xrightarrow{\text{thermal}} \mathrm{RO\cdot} + \mathrm{HO\cdot}
\end{aligned}$$

Since the first reaction is one between a hydrocarbon and diatomic oxygen, it is not feasible that this should lead directly to hydroperoxide formation from theoretical considerations. The second reaction, however, will proceed rapidly and should result in the formation of the hydroperoxide radical. For propagation, this latter radical must be sufficiently mobile so that it can abstract a hydrogen atom from a reactive center to form a hydroperoxide and generate a new free radical from the hydrocarbon. This is usually referred to as the chain-transfer step. The autocatalytic

[45] G. V. Schulz, *Chem. Ber.*, **80**, 335 (1947).

[46] J. L. Bolland and G. Gee, *Trans. Faraday Soc.*, **42**, 236 (1946).

[47] C. F. Cullis and C N. Hinshelwood, *Discussions Faraday Soc.*, **1947**, No. 2, 117.

[48] A. Robertson and W. A. Waters, *Trans. Faraday Soc.*, **42**, 201 (1946).

nature of such processes can be understood by the nature of the thermal splitting of the hydroperoxide which will produce two free radicals per hydroperoxide molecule, thus providing a source for the initiation and propagation of more chains.

It is apparent from such a mechanism that in order for these chains to be effective, there must be a high order of mobility in the system. The reaction chains otherwise may be terminated by recombination or other secondary reactions, thus slowing down or entirely stopping the oxidation process. From purely theoretical considerations then, it would appear that the autoxidation of alkali cellulose should proceed in a nonuniform fashion and occur preferentially in the amorphous region of the structure.

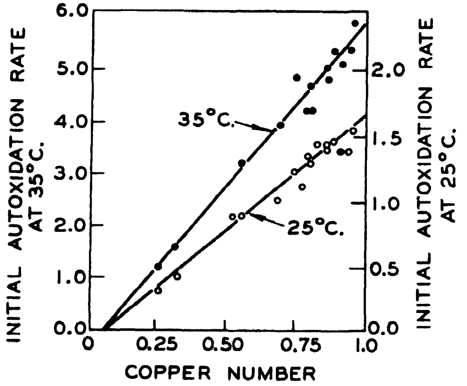

Fig. 11. Relation between initial autoxidation rate of alkali cellulose and the copper number of cellulose regenerated from it, for various commercial pulps (Entwistle, Cole, and Wooding[50]). The pulps were studied at a constant oxygen pressure of 700 mm. of mercury and at 25°C. and 35°C. Rates are expressed as ml. × 10^3 of O_2 (at normal temperature and pressure) per gram of cellulose per minute.

However, Samuelson[49] has studied the D.P. distribution of the aged alkali cellulose in comparison to purified linters, pulp prepared by bisulfite digestion, and pulp prepared by hypochlorite bleaching. His results indicate that both linters and aged alkali cellulose yielded the most uniform D.P. distribution, whereas hypochlorite bleaching gave the most uneven distribution, and bisulfite digestion occupied an intermediate position. The nature of the distribution was obtained by fractionation of the corresponding cellulose nitrates. From these distribution curves it can be concluded that "alkaline aging" (which is oxygen oxidation) is a remarkably uniform reaction and apparently will occur readily in the crystalline as well as the amorphous regions of the alkali cellulose.

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[49] O. Samuelson, *Svensk Kem. Tid.*, 59, 105 (1947).

Recently Entwistle[50] and coworkers have published the results of an excellent investigation of the kinetics of the autoxidation of alkali cellulose which has shed considerable light on the problem of the alkaline degradation of cellulose. The reaction was followed by measuring the oxygen absorption by various samples of alkali cellulose which, in the preliminary work, were prepared according to the usual viscose steeping procedure. The initial rates of reaction of these alkali celluloses were found to vary considerably but this difference practically disappeared once the oxidation reached the steady state.

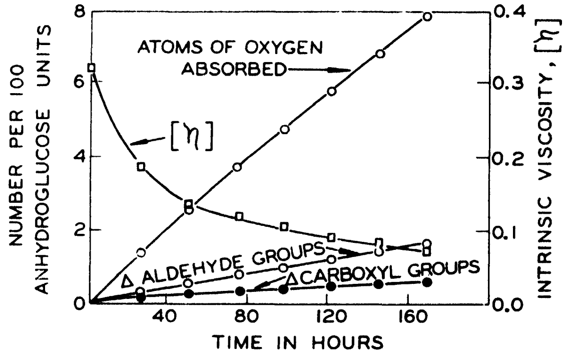

Fig 12 Functional group development during autoxidation of alkali cellulose pulp (Entwistle, Cole, and Wooding[50]) The intrinsic viscosity values are for cellulose in cuprammonium.

The deviation was explained when it was found that the initial rates of oxidation were a linear function of the copper number of the cellulose sample as shown in Figure 11 (p. 126). Thus it is possible to deduce the mechanism of the initiation reaction as follows:

$$R_{cell}CHO + O_2 \longrightarrow R_{cell}CO\cdot + \cdot HO_2$$

$$R_{cell}CO\cdot + O_2 \longrightarrow R_{cell}CO(OO\cdot)$$

$$R_{cell}CO(OO\cdot) + R_{cell}H \longrightarrow R_{cell}CO(OOH) + \cdot R_{cell}$$

The mechanism which has been proposed to explain this initiation through an aldehyde end group has been reasonably well verified. However, it holds only for the initiation reaction since all reaction between oxygen and cellulose does not occur at the terminal positions. If reactions were exclusively on aldehyde groups, the reduction in D.P. and changes in D.P. distribution would be not uniform but rather a progressive chopping up of those chains containing the most aldehyde groups. Secondly, since the decomposition of the peracids formed by the oxygen attack would produce carboxyl groups, then the number of such products should be closely equivalent to the number of oxygen atoms absorbed by the alkali cellulose.

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[50] D. Entwistle, E H. Cole, and N. S. Wooding, *Textile Research J.*, **19**, 527 (1949).

In Figure 12 a comparison is made between the oxygen absorption of alkali cellulose and the development of functional groups as well as the change in the intrinsic viscosity of the polymer. It is apparent from these data that carboxyl group formation is small and does not approach more than 10% of the total oxygen absorption. The change in intrinsic viscosity shows a curve typical of depolymerization reactions, which when replotted in the intrinsic fluidity form approximates a straight line; this supports the contention that the reaction is occurring uniformly throughout the alkali cellulose fibers.

The presence of active oxygen in the form of peroxides has been established in the oxidized alkali cellulose. The actual amount present at any given time is a function of the nature and amount of metallic contaminants such as iron or other metals with similar valence properties. For example, with one sample which contained a large proportion of iron, the decomposition of the peroxide was so rapid that the over-all peroxide concentration exhibited a maximum in the curve of peroxide concentration against time.

On the basis of these experimental facts it is possible to assign the following over-all mechanism to the oxidation of alkali cellulose:

$$\left.\begin{array}{l}
R_{cell}CHO + O_2 \longrightarrow R_{cell}CO\cdot + HOO\cdot \\
R_{cell}CO\cdot + O_2 \longrightarrow R_{cell}CO(OO\cdot) \\
R_{cell}CO(OO\cdot) + R_{cell}H \longrightarrow R_{cell}CO(OOH) + \cdot R_{cell}
\end{array}\right\}\text{Initiation}$$

$$\left.\begin{array}{l}
\cdot R_{cell} + O_2 \longrightarrow R_{cell}OO\cdot \\
R_{cell}OO\cdot + R_{cell}H \longrightarrow R_{cell}OOH + \cdot R_{cell}
\end{array}\right\}\text{Propagation}$$

$$\left.\begin{array}{l}
R_{cell}OOH \xrightarrow{\Delta} R_{cell}O\cdot + \cdot OH \\
R_{cell}H + \cdot OH \longrightarrow \cdot R_{cell} + HOH \\
R_{cell}O\cdot + R_{cell}H \longrightarrow \cdot R_{cell} + R_{cell}OH
\end{array}\right\}\text{Autocatalysis}$$

$$\left.\begin{array}{l}
\cdot R_{cell} + \cdot R_{cell} \longrightarrow R_{cell}{-}{-}R_{cell} \\
R_{cell}O\cdot + \cdot R_{cell} \longrightarrow R_{cell}OR_{cell} \\
R_{cell}O\cdot + R_{cell}O\cdot \longrightarrow R_{cell}OOR_{cell}
\end{array}\right\}\text{Possible termination reactions}$$

It must be emphasized that this reaction mechanism, as shown above, is merely a logical deduction from the experimental facts as they are known at present. It has not been completely proved, especially since the position of hydroperoxide substitution is not known, although the chain-initiation step is more thoroughly proved than the propagation one. From the complexity of this reaction the necessity for mobility within the alkali cellulose structure is more readily understood; in fact, such a reaction series requires essentially a homogeneous attack by the oxygen or an actual uniform solution of oxygen in all areas of the alkali cellulose. If such a solution is required, then it would be anticipated that the more swollen the cellulose structure is, the more readily would reaction occur. This condition was verified experimentally, and the rate was shown to be a function of the strength of the alkali used in preparing the alkali cellulose for alkali concentrations of 50% or less. Above this point the rate decreased with increasing caustic strength; this is probably the result of the greatly decreased mobility of the alkali, which prevents a uniform penetration of the cellulose and gives a very nonuniform product.

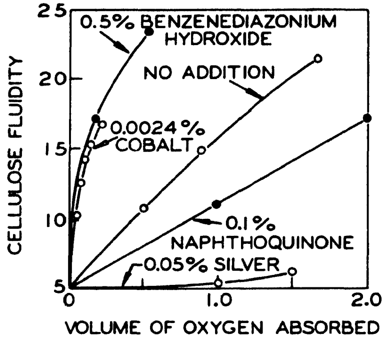

Fig 13 Effect of various catalysts and antioxidants on the depolymerization efficiency of alkali cellulose autoxidation (Entwistle, Cole, and Wooding[51]). The oxygen absorbed is plotted as milliliters (at normal temperature and pressure) per gram of cellulose. The fluidity values for cellulose were obtained in 1% solution in cuprammonium.

The autoxidation of alkali cellulose responds to positive and negative catalysis in a manner analogous to other chain reactions.[51] This is illustrated by Figure 13 in which typical positive catalysts such as cobalt and benzenediazonium hydroxide are compared with inhibitors such as naphthoquinone and metallic silver. From these data it is apparent that the reactions can be controlled by the proper choice of positive or negative catalyst.

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[51] D. Entwistle, E. H. Cole, and N S Wooding, *Textile Research J.*, **19**, 609 (1949).

In summary, then, the following general conclusions on oxidation of cellulose can be drawn:

1. The alkaline oxygen oxidation of cellulose is a reasonably uniform reaction which occurs by a hydroperoxide-type, free-radical mechanism.
2. The reaction is subject to catalysis by transition metals such as cobalt, iron, and manganese, and to retardation by silver and organic autoxidants.
3. Positive catalysis is accompanied by an increase in depolymerization per unit of oxygen absorption, whereas the opposite is true of negative catalysis.
4. Reducing-group production is increased by positive catalysts and reduced by retarders.

2. Hydrolytic Degradation

L. F. McBurney

Modification of cellulose by treatment with acids is one of its oldest known reactions, the first record of which appeared almost 100 years ago in an article by Calvert.[52] Girard[53] in 1875 reported the first of the systematic investigations of the effect of acids upon cellulose and, at the same time, proposed the name "hydrocellulose" to differentiate the products of hydrolysis from unmodified cellulose. The early literature in this field was well summarized in 1923 by Clifford.[54] It is interesting to note that at that time, after 58 years of research, he was unable to conclude whether or not hydrocellulose had a definite chemical composition. This indecision regarding the chemical nature of hydrocellulose was the result of a similar confusion over the structure of the parent cellulose, and disappeared with the general acceptance of the chain structure of the latter. Today it is almost universally agreed that hydrocelluloses are produced by the hydrolytic scission of the β-glucosidic chain bonds of cellulose and, as a result, the hydrocelluloses are chemically identical with the original cellulose, differing only in molecular size and distribution of degree of polymerization (D.P.).

[52] C. Calvert, *Pharm. J. Trans.*, [i.], **14,** 364 (1855).

[53] A. Girard, *Compt. rend.*, **81,** 1105 (1875).

[54] P. H. Clifford, *J. Textile Inst.*, **14,** T69 (1923).

(a) COURSE OF THE HYDROLYTIC REACTION

The chemistry and kinetics of cellulose hydrolysis are discussed in the preceding topic C-1 of this Chapter III, and for this reason the ensuing survey will be limited to the physical nature of the heterogeneous hydrolysis.

Hydrolysis of cellulose to glucose in solutions of strong acids is a rapid and complete reaction if recondensation of glucose is avoided. Heterogeneous hydrolysis on the other hand is very different; here the reaction proceeds rapidly at first but then becomes slower and appears almost to come to a standstill. The term "almost" is employed since hydrolysis does not cease, but continues at such a reduced rate that extremely long periods of time are required before further appreciable changes in physical properties are noted. The x-ray diagram remains unaltered during the reaction, and these observations led Davidson[55] to suggest that cellulose was composed of easily and difficultly penetrable phases. The difficultly penetrable (i.e., crystalline) region is responsible for the x-ray characteristics of cellulose, and since the diagrams do not change with heterogeneous hydrolysis, it was suggested that the hydrolyzing acids did not readily penetrate this portion of the molecule during hydrolysis. Hydrolysis therefore was depicted as occurring preferentially in the easily swollen,

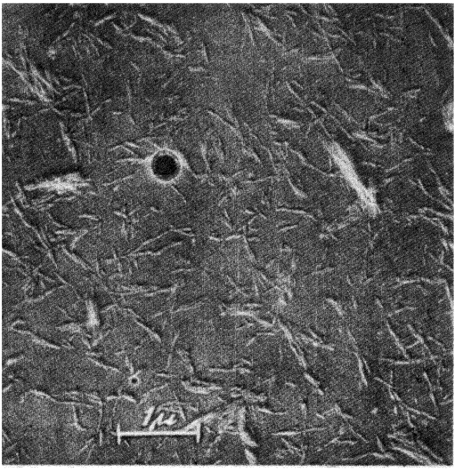

Fig. 14. Unhydrolyzed crystallites from wood cellulose (Rånby and Ribi[72]). These fibril fragments were obtained by hydrolysis with 2.5 *N* H_2SO_4 for 12 hrs. See p. 133.

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[55] G. F. Davidson, *J. Textile Inst.*, **34**, T87 (1943).

amorphous region of the fiber and as continuing rapidly so long as any of this region persisted. The disappearance of the amorphous region was signaled by a marked reduction in rate of hydrolysis, and cleavage continued only by the slow diffusion of the hydrolyzing acid into the crystalline region of the fiber. This concept served as an excellent qualitative explanation for the hydrolytic behavior of cellulose. The majority of the pertinent investigations during the past ten years have been concerned with attempts to assign numerical values to the relative crystalline to amorphous ratio in various celluloses by hydrolytic studies.[56–71]

The fraction of the cellulose remaining unhydrolyzed after the initial rapid reaction has terminated should be predominantly crystalline in nature, and measurement of its D.P. should serve to indicate the number of molecules in the crystalline region. Measurements of this type by Davidson,[55] Battista and Coppick,[64] and Nickerson and Habrle[61,63] have been in reasonable agreement, with the residues from cotton having D.P.'s in the range of 200–300 and those from regenerated cellulose having lower D.P.'s of about 100. The lower value from regenerated cellulose is expected since the crystalline region, having once been destroyed through solution, is not completely restored by precipitation. Rånby and Ribi[72] and Morehead[73] have provided optical proof for the existence and size of these crystallites by isolating them from hydrolyzates and by measuring their dimensions under the electron microscope. Rånby and Ribi found the crystallites from either

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[56] R. F. Nickerson, *Ind. Eng Chem., Anal Ed* , **13**, 423 (1941)

[57] R. F. Nickerson, *Ind. Eng Chem.*, **33**, 1022 (1941); **34**, 85, 1480 (1942).

[58] C. C. Conrad and A. G. Scroggie, *Ind Eng Chem.*, **37**, 592 (1945).

[59] R. F. Nickerson and J. A. Habrle, *Ind. Eng Chem.*, **37**, 1115 (1945).

[60] E. L. Lovell and O. Goldschmid, *Ind. Eng Chem.*, **38**, 811 (1946).

[61] R. F. Nickerson and J. A. Habrle, *Ind Eng. Chem.*, **38**, 299 (1946)

[62] F. C. Brenner, V. Frilette, and H Mark, *J. Am. Chem. Soc* , **70**, 877 (1948).

[63] R. F. Nickerson and J. A. Habrle, *Ind. Eng. Chem.*, **39**, 1507 (1947).

[64] O. A. Battista and S. Coppick, *Textile Research J.*, **17**, 419 (1947).

[65] V. I. Sharkov, V. S. Muromtsev, and G. D. Paramonova, *J. Applied Chem. (U S - S.R.)*, **21**, 1037 (1948); *Chem. Abstracts*, **43**, 5941 (1949).

[66] V. I. Sharkov, G. D. Paramonova, and M. N. Klikasheva, *J. Applied Chem (U.S.- S.R.)*, **21**, 1073 (1948); *Chem. Abstracts*, **43**, 5941 (1949).

[67] W. E. Roseveare, *Ind. Eng. Chem.*, **44**, 168 (1952).

[68] H. J. Philipp, M. L. Nelson, and H. M. Ziifle, *Textile Research J.*, **17**, 585 (1947).

[69] A. Meller, *J. Polymer Sci.*, **4**, 619 (1949).

[70] O. A. Battista, *Ind. Eng. Chem.*, **42**, 502 (1950).

[71] W. H. Algar, H. W. Giertz, and A. M. Gustafsson, *Svensk Papperstidn.*, **54**, 335 (1951).

[72] B. G. Rånby and E. Ribi, *Experientia*, **6**, 12 (1950).

[73] F. F. Morehead, *Textile Research J.*, **20**, 549 (1950).

native or regenerated cellulose to be from 500 to 600 A. long and from 50 to 100 A. wide, dimensions which would correspond to a D.P. of approximately 100. They also confirmed the fact that these isolated units had the same x-ray pattern as the original cellulose. These crystallites are illustrated in Fig. 14 (p. 131). Morehead reported somewhat different values for crystallite lengths, finding 1300–1500 A. for cotton, wood pulp, and ramie and 300 A. for regenerated cellulose. Despite these dimensional differences, the facts remain that the crystallites have sizes which are of the order expected from D.P. measurements and furthermore that they have actually been isolated and observed.

Up to this point in the discussion the impression would be obtained that the cellulose fiber is composed of definite crystalline and amorphous phases with relatively sharp lines of demarcation between them and that the ratio between these phases is amenable to experimental determination. This is an oversimplification of the true condition since there is a gradual transition between the highly organized and completely disorganized regions with no lines of sharp change (see Section B of Chapter IV). Hydrolysis in fact may actually increase the degree of organization of the cellulose[69,74,75] since chain rupture in the amorphous region will increase the mobility of the chain ends and permit them to realign themselves in a regular fashion. Recrystallization of cellulose during hydrolysis has received experimental verification by the investigations of both Ingersoll[74] and Howsmon,[75] who have shown that although the x-ray diagrams indicate no change in the crystal structure of cellulose, hydrolysis does greatly increase the definition of the pattern. The sharpening of the diagrams is achieved with only a slight loss in weight by the cellulose. This fact supports the recrystallization concept rather than the alternative explanation of the removal of the amorphous region by hydrolysis; the latter would also tend to increase the x-ray definition but only with an accompanying major weight loss.

The physical mechanism of heterogeneous hydrolysis can be summarized by saying that the hydrolyzing acid will rapidly penetrate the disorganized regions of the fiber and bring about chain scission in these regions. This chain rupture will be accompanied by some crystal growth due to the increased mobility of the chain ends, and as a result the amount of highly organized cellulose will be increased. Once all the amorphous region has been destroyed the reaction will become extremely slow because penetration of the acid into the crystallites is difficult, and for most purposes the reaction can be considered to approach a "leveling-off" value of D.P.

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[74] H. G. Ingersoll, *J. Applied Phys.*, **17**, 924 (1946).

[75] J. A. Howsmon, *Textile Research J.*, **19**, 152 (1949).

The position of this leveling-off point will be a function of the past history of the cellulose, being high for native cotton or ramie and low for regenerated celluloses.

(b) PROPERTIES OF HYDROCELLULOSES

The preponderance of work in the field of cellulose hydrolysis has served to show that the primary reaction is a cleavage of the 1,4-glucosidic bonds with the result that the hydrocelluloses thus formed have lower average D.P.'s. On this basis it would be anticipated that those physical properties which are a function of chain length would show changes whose magnitude would be related to the severity of hydrolysis. Two of the industrially important cellulose properties, strength and viscosity, are the direct result of chain length and as a result will undergo drastic changes during hydrolysis.

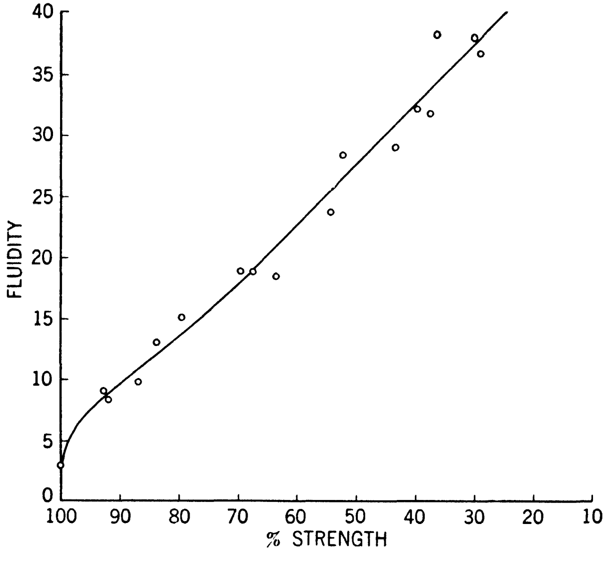

Fig. 15. The relation between breaking strength and fluidity of hydrocelluloses (Clibbens and Ridge[78])

The fluidity of solutions of cellulose in cuprammonium increases (i.e., viscosity decreases) as hydrolysis proceeds. Since fluidity and strength are direct functions of chain length, it would be expected therefore that a definite correlation would exist between these properties. This relationship has been pointed out by several investigators[76–79] and is illustrated in Figure 15. These data were obtained from a variety of treatments on a single sample of cotton yarn and serve to show the independence of the results on the method of hydrolysis. It is seen that the variation of strength with fluidity is essentially linear over the major portion of the measured range. The existence of such a correlation is indicative of a relatively uniform attack by the hydrolyzing acid as opposed to the localized degradation observed in microbiological attack where considerable loss of strength is obtained with little apparent change in the fluidity of the residue. If hydrolysis is extended beyond the point illustrated in Figure 15, the cellulose begins to lose its fibrous structure and is reduced to a friable powder, with complete loss in tensile strength being observed at fluidities of 44 or above.

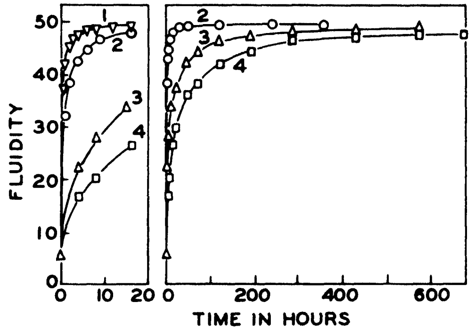

Fig. 16 Change in fluidity of cellulose during acid hydrolysis (Davidson[65]). Hydrolytic conditions: (1) 0.5 *N* H_2SO_4 at 100°C ; (2) 10 *N* HCl at 20°C.; (3) 6 *N* HCl at 20°C.; (4) 10 *N* H_2SO_4 at 20°C. Fluidity values are those of the resulting hydrocelluloses in 0.5% cuprammonium solution.

The change in fluidity with time of treatment and conditions under which hydrolysis is carried out is illustrated in Figure 16. These data show that the rate at which hydrolysis occurs is a function of the hydrolyzing acid, its concentration, and the temperature of the reaction; the ultimate leveling-off point, however, is approximately the same in each case which shows that the mechanism is independent of these variables. The leveling-off point will not be the same for different celluloses since, as pre-

[76] C. Birtwell, D. A. Clibbens, and A. Geake, *J. Textile Inst.*, **17**, T145 (1926).

[77] F. D. Farrow and S. M. Neale, *J. Textile Inst.*, **15**, T157 (1924).

[78] D. A. Clibbens and B. P. Ridge, *J. Textile Inst.*, **19**, T389 (1928).

[79] R. T. Mease and I. F. Gleysteen, *J. Research Natl. Bur. Standards*, **27**, 543 (1941)

viously discussed, it is a function of the past history of the sample. This observation is illustrated by Figure 17 where the fluidity variations with time during hydrolysis of mercerized and unmercerized cotton are compared at the same temperature and acid concentrations.[80]

The mercerized cellulose in this illustration shows a fluidity–time curve which is similar in shape to that of the unmercerized sample, but both the rate of change and the leveling-off point are greater. These facts lead to the conclusion that the hydrolysis mechanism is the same in both cases; the only difference is that the ratio of ordered to disordered region is less in the mercerized cellulose than in the unmercerized sample.

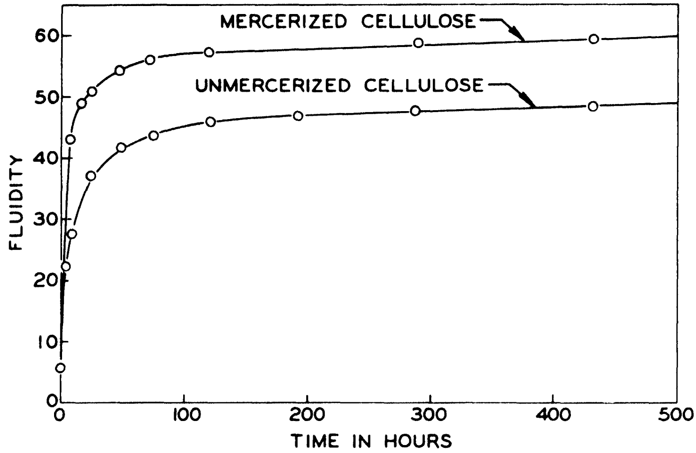

Fig. 17 Hydrolysis of cellulose with 6 N HCl at 20°C (compiled from data of Davidson[80]). Fluidity values are those of the resulting hydrocelluloses in 0.5% cuprammonium solution.

Hydrolytic cleavage of cellulose results in the formation of two new end groups, one of which will be reducing in nature and the other nonreducing. It would be expected therefore that the copper number of hydrocellulose would show an increase with hydrolysis and would be a direct function of the amount of reducing end groups formed.[76] This hypothesis can be further extended to say that there should be a linear relationship between the aldehyde content and fluidity for hydrocelluloses since the latter is an approximate measure of the number of chain breaks which have occurred, each of which will produce one reducing (i.e., potential aldehyde) end group. The predicted linear relationship between fluidity[81] and aldehyde content is supported by the data in Figure 18.

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[80] G. F. Davidson, *J. Textile Inst.*, **34**, T95 (Table II), T96 (Table IV) (1943).

The use of copper number to determine the reducing value of hydrocelluloses is reasonably satisfactory for the fibrous material but is of much less value in the case of the extensively modified powdery products. It has been found[55] that with the latter materials copper number determinations are experimentally inconvenient because of the extremely long reaction periods required.

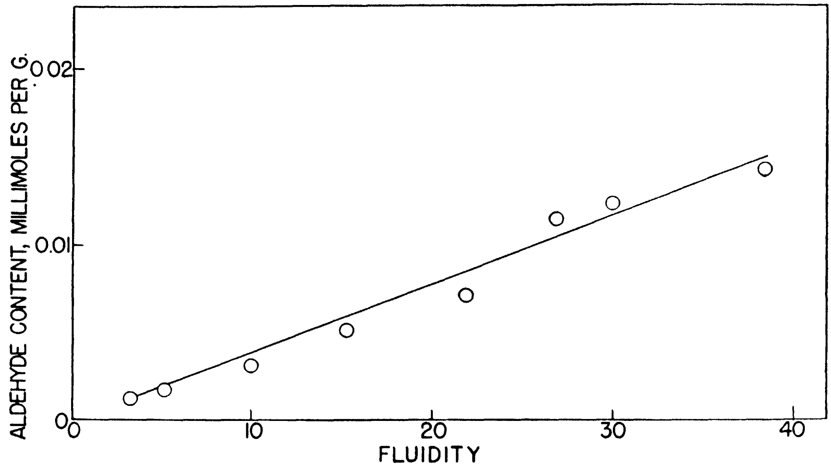

Fig 18 Relation of aldehydic content of hydrocelluloses to fluidity (Martin, Smith, Whistler, and Harris[81]).

The acid hydrolysis of cellulose yields products which are unstable toward hot dilute alkalies, under which conditions water-soluble components are produced with a resultant loss of weight by the hydrocellulose. In the early stages of hydrolysis the loss in weight is proportional to the copper number. The weight loss is rapid initially but becomes progressively slower as hydrolysis proceeds and eventually becomes essentially constant. This leveling-off point appears at a weight-loss value of approximately 50%. In the early stages of reaction (i.e., while the product retains its fibrous nature[76]) the relationship between weight loss and fluidity has been shown to be independent of hydrolytic conditions. This generalization can be extended to cover the entire range including the powdery materials[55] as shown in Figure 19. For four series of hydrocelluloses it is seen that the relationship between weight loss and fluidity can be represented by a single curve which shows the generality of the correlation. With the mercerized hydrocellulose the maximum value of weight loss does not differ appreciably from that of the unmercerized hydrocelluloses; however, the fluidity of the former is much greater so that the fluidity–weight-loss relationships are not identical for the two types.

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[81] A. R. Martin, L. Smith, R. L. Whistler, and M. Harris, *J. Research Natl. Bur. Standards*, **27**, 449 (1941); *Am. Dyestuff Reptr.*, **30**, 628 (1941).

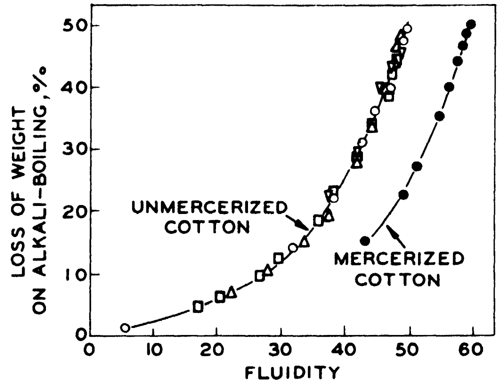

Fig. 19. Alkaline instability of hydrocelluloses (Davidson[55]) Hydrolytic conditions: for unmercerized cotton—

∇ 0.5 N H_2SO_4 at 100°C.
○ 10 N HCl at 20°C
△ 6 N HCl at 20°C.
□ 10 N H_2SO_4 at 20°C.

for mercerized cotton—

● 6 N HCl at 20°C.

Alkali-boil: 1% NaOH for 6 hrs. at 100°C. Fluidity measured in 0.5% cuprammonium solution.

The maximum solubility of hydrocellulose at ordinary temperatures occurs in 3 N NaOH, and it falls off rapidly with increasing or decreasing alkali concentration. This maximum is dependent upon temperature and will, for example, occur at 2.5 N at −5°C.[82]

Fibrous hydrocelluloses were shown to be less hygroscopic[83] than the original cotton, and Davidson[55] has extended this observation to the powdery modifications. The relative moisture absorption (i.e., the ratio of absorptive capacity of hydrocellulose to parent cellulose) of the hydrocellulose is independent of acid concentration in the early stage of reaction but does show a considerable dependence at the later stages of hydrolysis. This observation is illustrated in Figure 20 where the effect of 6 *N* and 10 *N* HCl is compared. The treatment with 6 *N* HCl results in a rapid initial decrease in relative moisture absorption which then levels off and becomes essentially constant at the later stages. With 10 *N* HCl on the other hand, the initial decrease is followed by an increase in the ratio which appears eventually to reach a maximum value. A decrease in relative moisture absorption ratio would be anticipated since the amorphous region of the fiber is most easily penetrable by water, and thus as it is destroyed the amount of water which the fiber is capable of absorbing would be reduced.

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[82] G. F. Davidson, *J. Textile Inst.*, **25**, T174 (1934).

[83] A. R. Urquhart, W. Bostock, and N. Eckersall, *J. Textile Inst.*, **23**, T135 (1932).

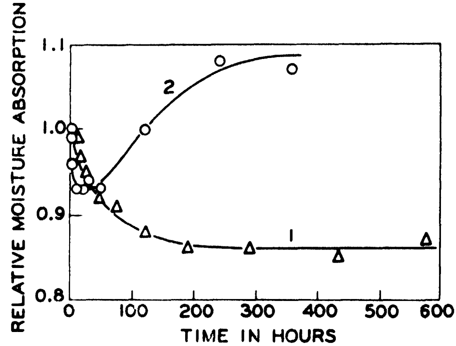

Fig 20. Change in hygroscopicity of cellulose during acid hydrolysis (Davidson[55]) Hydrolytic conditions: (1) 6 *N* HCl and (2) 10 *N* HCl at 20°C The relative moisture absorption is the ratio of the amount of moisture absorbed by the hydrocellulose to that absorbed by the unmodified cotton under the same conditions of temperature and relative humidity.

The behavior of the product formed by the reaction of 10 *N* HCl is, however, unexpected and may be the result of swelling which has been shown to accompany this treatment. In this latter case the hydrocelluloses so produced are gelatinous when wet and hard and horny when dried, properties which are explainable on the basis of considerable swelling having occurred during the reaction.

To summarize the properties of hydrocelluloses it can be said that the reaction of cellulose with acids under heterogeneous conditions brings about a progressive increase in fluidity, a loss of strength, and the production of reducing groups. A stage is ultimately reached beyond which little further deterioration of properties is observed; this leveling-off point occurs when only a small proportion of the glucosidic bonds in the cellulose chain are cleaved. The hydrolytic reaction has not ceased at this point however, as evidenced from loss-of-weight measurements which indicate a continuation of the reaction at a greatly reduced rate. The enhanced rate of degradation of mercerized cellulose over unmercerized cellulose is explained by the larger proportion of accessible or disorganized structure in mercerized cellulose. All of these observations, combined with the moisture absorption behavior, support the conclusion that reaction is in the main confined to the amorphous region of the fiber during heterogeneous hydrolysis.

3. Oxidative Degradation

L. F. McBurney

Cellulose, because of its polyhydric alcohol structure, is very sensitive to oxidizing media. The extensive modifications which accompany this reaction give rise to products whose chemical and physical properties depend upon the oxidizing reagent used, and the acidity or basicity of the medium in which oxidation occurs. The early literature in this field was largely of an empirical nature and of a character which made chemical interpretations difficult. Because of this fact, as well as the existence of an excellent summary by Clifford and Fargher,[84] this early work will be excluded from the present review.

Cellulose oxidation is a process of considerable economic importance, the value of which cannot be overemphasized. At some point in their history all commercial celluloses have been exposed to an oxidizing environment, and in most cases the extent of this exposure regulates the future utility of the product. Bleaching reactions, which are utilized in the manufacture of all types of cellulose, are oxidation reactions. In this treatment attempts are made to control the action of the bleach so that only the colored impurities are affected and made amenable to a subsequent solvent extraction. If, however, control is not sufficiently close, the cellulose fibers will be attacked and tendered because of oxidative degradation. The extreme sensitivity of cellulose to air oxidation in the presence of alkali has been described in a previous section (see topic 1 of this Section C, Chapter III) where it was indicated that the reaction is employed to regulate the ultimate strength of regenerated fibers. This alkaline-catalyzed oxidation of cellulose plays an equally important part in all cellulose processes that require an alkali cellulose as an intermediate.

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[84] P. H. Clifford and R. G. Fargher, *J. Textile Inst.*, **13**, T189 (1922).

(a) FACTORS CONTROLLING CELLULOSE OXIDATION[85]

The properties of any oxidized cellulose depend upon the method by which it is prepared. The term *oxycellulose,* which has been used extensively in the literature to characterize these oxidized products, implies a specificity of structure which is not achievable and for this reason the term *oxidized cellulose*[86] is preferred. In neutral or acidic solutions, oxidized celluloses of the reducing type are formed (i.e., they show a high content of reducing groups as measured by the copper number method), whereas in alkaline solutions, the acidic type of oxidized cellulose is formed. The latter has sometimes been referred to as the "methylene blue" type since it

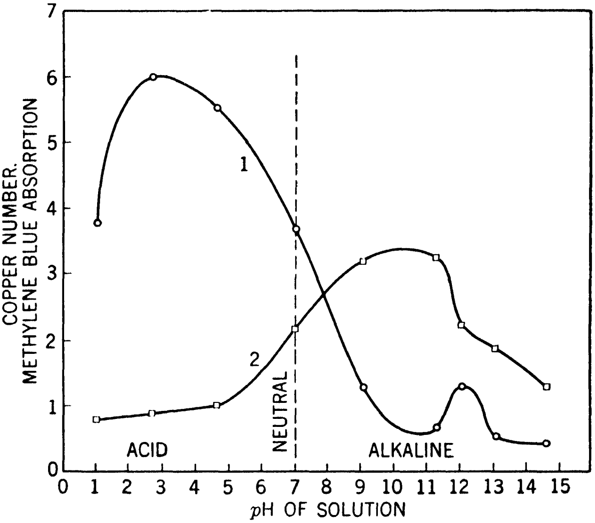

Fig. 21 Influence of hydrogen-ion concentration of the oxidizing agent (hypochlorite) on the formation of reducing and acidic groups in cellulose (Birtwell, Clibbens, and Ridge[87]). Curve 1; copper number; Curve 2; methylene blue absorption.

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[85] The discussion of this topic is based on that prepared by Henry A. Rutherford and Milton Harris for the first edition of this book (pp. 176–179).

[86] C. C. Unruh and W. O. Kenyon, *Textile Research J.*, **16**, 1 (1946).

exhibits rather high affinity for methylene blue. Acidic oxidized celluloses tend to show high retention of alkali presumably due to the presence of carboxylic acid groups.[87-89]

The manner in which hydrogen-ion concentration may influence the type of oxidized cellulose obtained is shown in Figure 21. The rate of formation of oxidized cellulose is considerably influenced by pH, the most rapid reaction for most oxidants occurring at or near the neutral point as indicated by the data in Figures 22, 23, and 24. The data emphasize the fact that the rate or extent of oxidation is not necessarily ascertained by the measurement of the change in any one given property such as copper number or methylene blue absorption; thus, as indicated by the copper number method, the rate is greater at pH 4.6 than at pH 11.2, whereas, as indicated by methylene blue absorption, the effects of pH appear to be reversed.

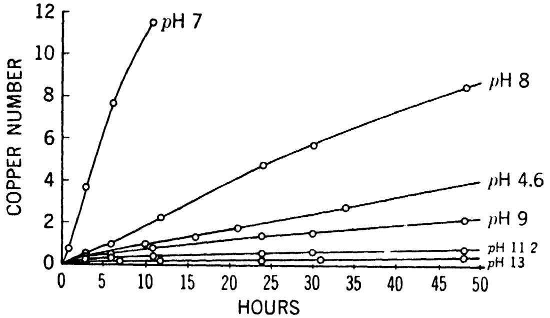

Fig. 22. The effect of pH on the rate of increase of copper number (Clibbens and Ridge[90]): 0.04 *N* sodium hypochlorite at 25°C.; ratio of cotton to solution, 1·100

The rate of formation of oxidized cellulose is also influenced by temperature, concentration of oxidant, and the nature of the oxidizing reagent itself. As an example of the last, hypobromite is much more effective for a given set of conditions than hypochlorite.[90] Finally, the rate of oxidation of the cellulose may be greatly accelerated by the simultaneous oxidation of a third substance in the system. Thus, oxidation with dichromate in the presence of oxalic acid is far more rapid than in the presence of sul-

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[87] C. Birtwell, D. A. Clibbens, and B. P. Ridge, *J. Textile Inst.*, **16**, T13 (1925).

[88] G. F. Davidson, *J. Textile Inst.*, **32**, T132 (1941).

[89] H. A. Rutherford, F. W. Minor, A. R. Martin, and M. Harris, *J. Research Natl Bur. Standards*, **29**, 131 (1942).

[90] D. A. Clibbens and B. P. Ridge, *J. Textile Inst.*, **18**, T135 (1927).

furic acid.[90] As another example, it has been shown that when cotton, on which a reduced vat dye has been absorbed, is treated with hypochlorite,

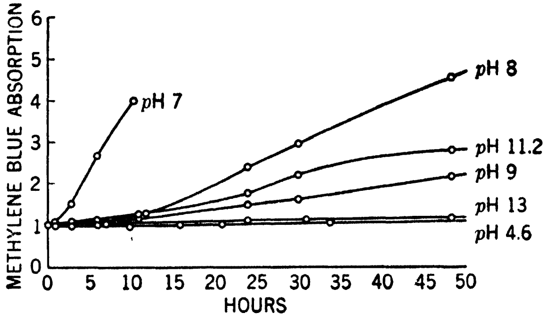


Fig. 23. The effect of pH on the rate of increase of methylene blue absorption (Clibbens and Ridge[90]): 0.04 *N* sodium hypochlorite at 25°C.; ratio of cotton to solution, 1:100.

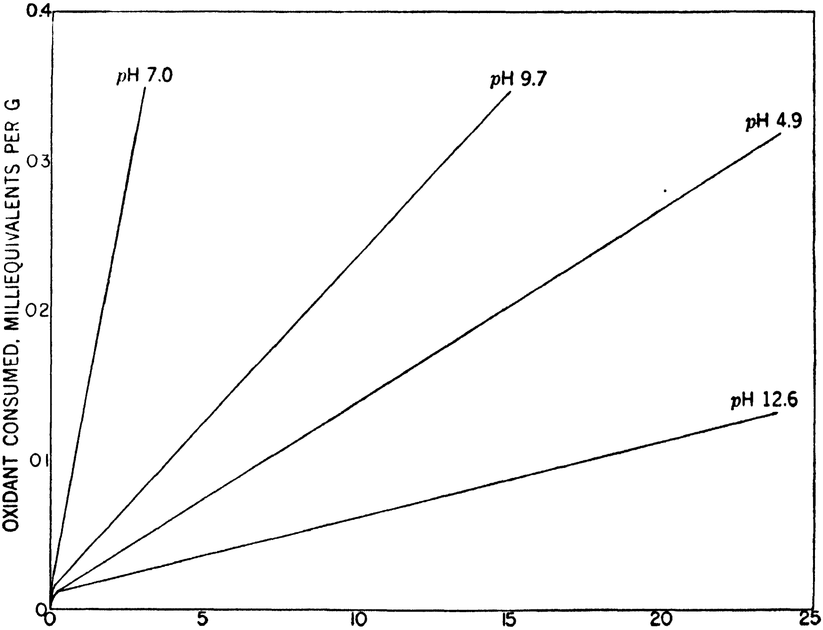


Fig. 24. The effect of pH on the rate of consumption of active chlorine (Rutherford, Minor, Martin, and Harris[89]). Conditions: 3 g./liter of available chlorine; 25°C.; ratio of cotton to solution, 1:100.

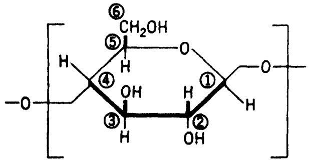
the oxidation of the cellulose is greatly accelerated.[91,92] The method of oxidation with dichromate in the presence of oxalic acid has been suggested as a very convenient one for the preparation of an oxidized cellulose of the extreme reducing type.

Although many oxidizing agents tend to follow this same general trend in respect to pH, potassium permanganate is outstandingly different. The maximum rate of oxidation of cellulose by this substance occurs at pH 11.2 and the minimum at pH 9, the latter value being one at which a marked transition in the nature of the oxidized cellulose occurs.[93] In contrast with hypochlorite, little change in the type of oxidized cellulose formed with this reagent occurs between pH 5 and 9.

(b) COURSE OF REACTION OF CELLULOSE WITH DIFFERENT OXIDIZING REAGENTS

(1) *Chemical Nature of the Oxidative Reaction*

The oxidation of cellulose has been the subject of a voluminous literature over the years, and these investigations have led to the accumulation of quantities of empirical information concerning properties and possible courses of reaction. In spite of all this work, very few concrete facts have come to light concerning the how and where of oxidative attack on cellulose. In fact the term *oxycellulose,* which would appear to signify an individual chemical species, is a misnomer since the products resulting from oxidation are best described as a family of copolymers of glucose and oxidized glucose of indefinite structure. The reason for the heterogeneous nature of oxidized cellulose can best be appreciated by considering what can happen during oxidation of an individual anhydroglucose unit, the formula of which is:



Anhydroglucose unit of cellulose
(Specifically anhydroglucopyranose unit)

From an examination of this formula it is apparent that there could be six major types of attack in the molecule.

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[91] H. A. Turner, G. M. Nabar, and F. Sholefield, *J. Soc. Dyers Colourists,* **51,** 5 (1935).

[92] G. M. Nabar, F. Sholefield, and H. A. Turner, *J. Soc. Dyers Colourists,* **53,** 5 (1937)

[93] C. Dorée and A. C. Healey, *J. Soc. Dyers Colourists,* **49,** 290 (1933).

1. Attack on carbon atom 1. This has been shown to occur only on terminal anhydroglucose units and generally is of minor importance unless the oxidation is occurring in strongly acidic medium where hydrolytic cleavage of the chain is occurring. It is of major importance in the alkaline aging reaction of alkali cellulose where the terminal group is the point of initiation of the reaction.[94] Oxidation at position 1 would result in the formation of a carboxyl group to give an acidic oxidized cellulose.
2. Attack at the 2- and 3-hydroxyl groups, either simultaneously or individually, to form carbonyl groups without ring cleavage. In this case an oxidized cellulose of high reducing value would be produced.
3. Attack at the 2- and 3-hydroxyl groups simultaneously with subsequent ring cleavage to form aldehyde groups, again leading to a reducing type of oxidized cellulose.
4. Attack on the aldehyde groups produced by reaction 3 to convert them into carboxyl groups, thus resulting in an acidic type of oxidized cellulose.
5. Attack at position 6 to form an aldehyde group which yields a reducing-type oxidized cellulose.
6. Attack at position 6 to form a carboxyl group which yields an acidic-type oxidized cellulose.

From the multiplicity of possible products it is easily understood why so much confusion has arisen over the nature of oxidized cellulose, and also why the term *oxycellulose* implies a specificity that is not inherent in most of the products. In order to assign accurately the course of reaction of a nonspecific oxidant with cellulose, analytical tools are required which not only measure the amounts of functional groups present but also show their positions in the molecule. Such analytical procedures are yet to be developed, and thus our knowledge of the reactions remains uncertain.

The oxidized celluloses have been divided, as mentioned previously, into two general classes which are dependent upon their acidic or reducing character. Such a grouping is satisfactory from the utility viewpoint; on the basis of theoretical knowledge of the nature of oxidized cellulose, however, another classification is more helpful. Here again two types can be distinguished. The first and more important type contains only those materials which have the nature of a reproducible chemical individual. These oxidized celluloses are the result of the attack on specific hydroxyls in the molecule by oxidants such as periodic acid, lead tetraacetate, and possibly nitrogen dioxide (N_2O_4). The second type contains all other oxidized celluloses which are indefinite in structure and result from nonspecific reactions with reagents such as permanganate, chromic acid, hydrogen peroxide, and hypochlorites.

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[94] D. Entwistle, E. H. Cole, and N. S. Wooding, *Textile Research J.*, **19**, 527 (1949).

The earlier investigators assumed that the primary alcoholic group in position 6 was most vulnerable to oxidative attack and was converted into carboxyl. The chain degradation which accompanied this oxidation was thought to be a direct scission of the glucosidic linkages by the oxidant. Such conclusions were based upon the production of carbon dioxide from oxidized celluloses when boiled with hydrochloric acid, a reaction typical of uronic acids and one which would be expected from the copolymer of polyanhydroglucuronic acid and polyanhydroglucose resulting from the oxidation of the primary alcohol group.

As a result of the work of Clibbens and Ridge[95] and Davidson,[96-98] it became apparent that chain degradation accompanying some types of cellulose oxidation is not the result of direct scission of the molecular chain but is the result of the formation in the molecule of a chemically labile group which is sensitive to alkaline cleavage. The confirmation of the belief that chain degradation of oxidized celluloses is the result of alkaline instability[99] was obtained by a comparison of the fluidities of nitrated oxidized celluloses in an organic solvent with the fluidities of the corresponding celluloses in cuprammonium. It was observed that oxidized cellulose which was not exposed to alkali could be nitrated in a nondegrading medium, and the nitrates so obtained had fluidities which showed only a small increase over those of the unoxidized starting material. The cuprammonium fluidity of the oxidized cellulose, on the other hand, was much greater than that of the unoxidized cellulose. This difference in nitrate and cuprammonium fluidity could only be the result of depolymerization which occurs in the highly alkaline cuprammonium medium and is not the result of a direct chain scission by the oxidant. This alkali sensitivity was quite marked for products prepared by the periodate oxidation of cellulose[100] as can be seen by reference to Figure 25.

In this illustration nitrocellulose fluidity is plotted against the extent of treatment of the oxidized cellulose with alkaline solution prior to nitration. From these curves it is apparent that even very mild alkalies such as 0.05 *M* borax at 20°C. (curve 1) cause considerable rise in fluidity, and that strong alkalies such as 0.1 *N* NaOH (curve 3) produce a rapid depolymerization of the compound. On the other hand, alkaline treatment (0.1 *N* NaOH) has little effect on the cuprammonium fluidity of an oxidized cellulose as can be seen from curve 3A.

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[95] D. A. Clibbens and B. P. Ridge, *J. Textile Inst.*, **19**, T389 (1928).

[96] G. F. Davidson, *J. Textile Inst.*, **29**, T195 (1938).

[97] G. F. Davidson, *J. Textile Inst.*, **25**, T174 (1934).

[98] G. F. Davidson, *J. Textile Inst.*, **27**, P144 (1936).

[99] G. F. Davidson, *J. Soc. Dyers Colourists*, **56**, 58 (1940).

[100] G. F. Davidson, *J. Textile Inst.*, **31**, T81 (1940).

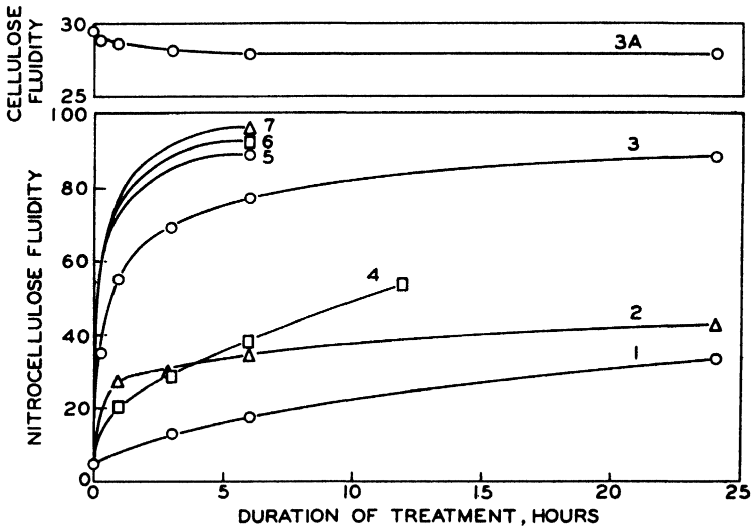

Fig. 25. Effect of alkaline treatments of periodate-oxidized celluloses as measured by the fluidities of their nitration products (Davidson[100]). Curves 1–7: effect on nitrocellulose fluidity of treatment with (1) 0.05 *M* borax at 20°C.; (2) ammonia, 200 g./liter at 20°C.; (3) 0.1 *N* NaOH at 20°C.; (4) water at 100°C.; (5) 1% soap at 100°C.; (6) 0.1 *M* Na_2CO_3 at 100°C.; (7) 0.25 *N* NaOH at 126°C. Curve 3A: effect on cellulose fluidity of treatment with 0.1 *N* NaOH at 20°C.

(2) *Alkaline Depolymerization of Oxidized Celluloses*

Studies of the reaction between cellulose and periodates have been of great value in clarifying the alkaline instability of oxidized celluloses since the reaction is specific in nature and the chemical changes undergone by the cellulose molecule are understood.

Periodic acid (or potassium paraperiodate) oxidizes 1,2-glycols and converts them into the corresponding aldehydes. Jackson and Hudson[101] applied this reagent to cellulose and established that the 2- and 3-hydroxyl groups were oxidized to aldehyde groups with a carbon–carbon bond cleavage. Thus:

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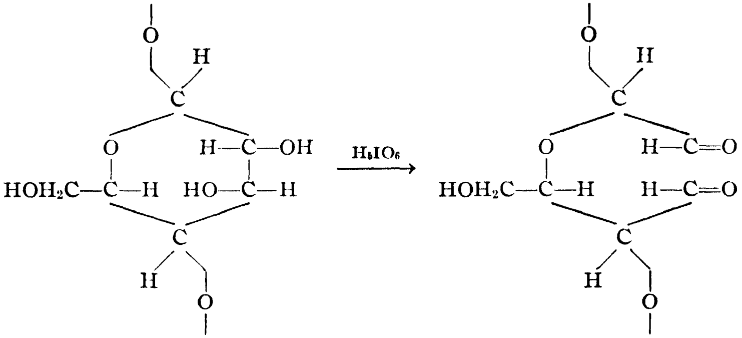
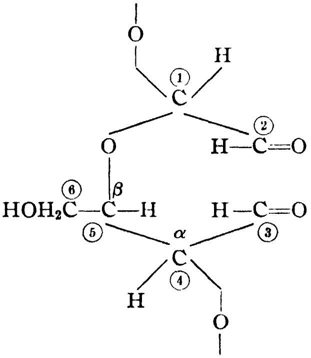
[101] E. L. Jackson and C. S. Hudson, *J. Am. Chem. Soc.*, **58**, 378 (1936); **59**, 994, 2049 (1937); **60**, 989 (1938).



An examination of the structure of periodate-oxidized cellulose leads to the question: What is peculiar about this arrangement that confers alkaline instability to the molecule? If the essential portion of the oxidized structure is written as follows:



it is apparent that the oxygen of the original ring ether is in a position which is beta to the aldehyde group produced from the 3-hydroxyl. Helferich and Lutzmann,[102] in their investigation of the alkaline behavior of glucosidic groups which are beta to strongly electronegative groups, found that glucose will be rapidly split off under these conditions and the rate of scission can be measured by the reduction of Fehling solution. This observation is illustrated by the following example from Helferich's work (where Gl is a glucosyl group):

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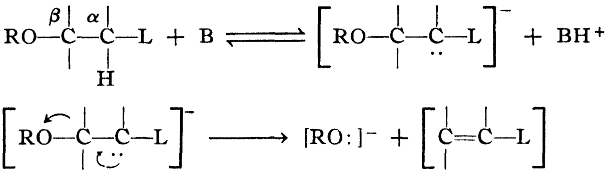
[102] B. Helferich and H. Lutzmann, *Ann.*, **541**, 1 (1939).

$$\mathrm{Gl{-}OCH_2CH_2NO_2} \xrightarrow{[\mathrm{OH}]^-} \text{Glucose} + \text{nitroethane polymer}$$

Further work by Helferich[103,104] and others[105–111] has shown this to be a single example of a general reaction of ethers for which the mechanism has been established as follows:



$$\mathrm{RO{-}\overset{\beta|}{\underset{|}{C}}{-}\overset{\alpha|}{\underset{|\atop H}{C}}{-}L} + \mathrm{B} \rightleftharpoons \left[\mathrm{RO{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{\cdot\cdot}{C}}{-}L}\right]^- + \mathrm{BH^+}$$

$$\left[\mathrm{RO{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{\cdot\cdot}{C}}{-}L}\right]^- \longrightarrow [\mathrm{RO{:}}]^- + \left[\mathrm{\overset{|}{\underset{|}{C}}{=}\overset{|}{C}{-}L}\right]$$

$$[\mathrm{RO{:}}]^- + \mathrm{BH^+} \longrightarrow \mathrm{ROH} + \mathrm{B}$$

This cleavage requires the presence of a strongly electronegative group L which by means of an inductive effect makes the hydrogen on the α-carbon atom acidic enough to be removed by a strong base B. It is also necessary that the electronegative group and the ether linkage are separated by exactly two carbon atoms for scission to occur. Thus, alkaline cleavage can occur if the ether linkage is separated by two carbon atoms from an electronegative group, and the α-carbon atom has at least one hydrogen atom attached to it.

Haskins and Hogsed[112] have applied this aldol dehydration mechanism to explain the alkaline instability of periodate-oxidized cellulose as shown on the next page. In this case the hydrogen on the α-carbon atom is removed by the base; this is followed by an electron shift to form a double bond between the α- and β-carbon atoms with a simultaneous carbon–oxygen scission. The cleavage which occurs results in a chain break in the molecule and a corresponding increase in fluidity. An alternative explanation for the alkaline instability has been proposed[113] which depicts the aldehyde type of oxidized cellulose as a negatively substituted ketene acetal. If this were the case, the acetal would undergo a rapid hy-

[103] B. Helferich and M. Hase, *Ann.*, **554**, 261 (1943).

[104] B. Helferich and H. Schnorr, *Ann.*, **547**, 201 (1941).

[105] C. R. Hauser and D. Breslow, *J. Am. Chem. Soc.*, **62**, 3344 (1940).

[106] B. H. Nicolet, *J. Am. Chem. Soc.*, **53**, 4458 (1931).

[107] R. Kuhn and I. Löw, *Ber.*, **74B**, 219 (1941).

[108] H. S. Isbell, *Ann. Rev. Biochem.*, **12**, 214 (1943).

[109] R. T. Arnold, N. Bortnick, and E. McMullen, *J. Am. Chem. Soc.*, **64**, 1410 (1942).

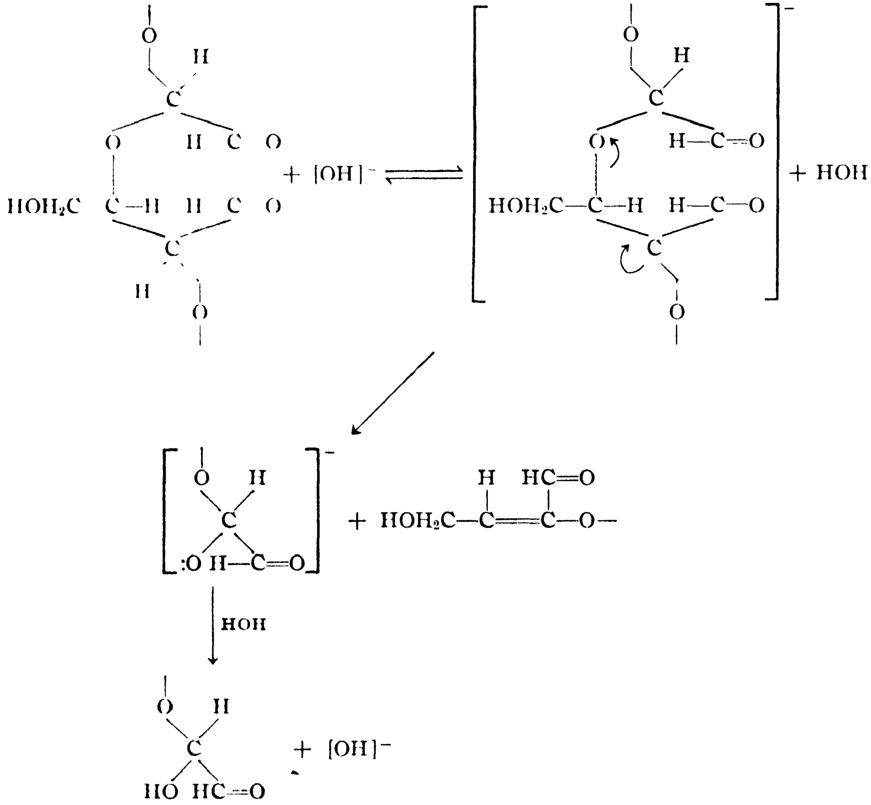
[110] L. F. McBurney, Dissertation, Univ. of Pennsylvania, June, 1942.

[111] D. Chaney, Dissertation, Univ. of Pennsylvania, June, 1942.

[112] J. F. Haskins and M. J. Hogsed, *J. Org. Chem.*, **15**, 1264 (1950).

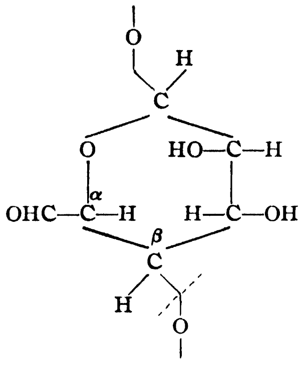
[113] E. Pacsu, *Textile Research J.*, **15**, 354 (1945).

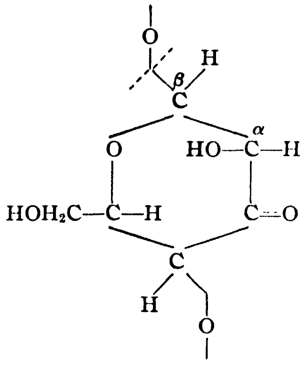
drolysis in alkaline medium to form an ester of glycolic acid by a carbon-oxygen cleavage. The ester thus formed then would be susceptible to the normal alkaline hydrolysis of esters. This mechanism appears unduly complicated and lacks the experimental verification that has been developed for the beta cleavage of ethers.

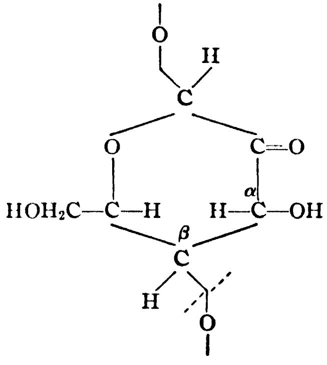


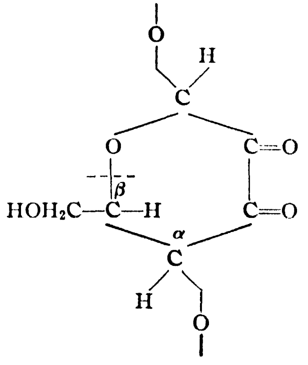
These studies have also served to indicate that weak or labile links can be *introduced* into the cellulose molecule. The presence of such links will depend, however, entirely upon the degree to which the cellulose has been oxidized; they are not inherent in the structure of the native fiber. Furthermore, they are only weak links in the presence of alkali and show remarkable stability in acid solution[113] as indicated by their ability to withstand 2 *N* HCl. Their positions along the molecular chain will not be regular but rather they will occur in a random fashion depending upon the degree of oxidation and the type of oxidant.

In the case of the alkaline sensitivity of those oxidized celluloses which are formed by the action of nonspecific oxidants on cellulose, the same mechanism is equally applicable. If the possibility of the formation of mixed derivatives is neglected, the following four structures are possible as a result of direct oxidation:


O
H
C
O
HO—C—H
α
OHC—C—H
H—C—OH
β
C
H
O


O
H
β
C
α
O
HO—C—H
HOH₂C—C—H
C=O
C
H
O


O
H
C
O
C=O
α
HOH₂C—C—H
H—C—OH
β
C
H
O


O
H
C
O
C=O
β
HOH₂C—C—H
C=O
α
C
H
O

In every case the strongly electronegative carbonyl group is beta to an ether oxygen, and a hydrogen atom is attached to the α-carbon atom; thus, the system required for alkaline cleavage is maintained and therefore scission would occur at the bonds indicated by the broken lines in the above formulas. Although the aldol dehydration mechanism was originally proposed to explain the alkaline cleavage[112] of periodate-oxidized cellulose, it is equally applicable to any oxidized cellulose containing carbonyl groups in the positions illustrated above.

Up to this point in the discussion it has been emphasized that a certain few oxidants, for example periodic acid (or its sodium or potassium salt) and lead tetraacetate, have a specific attack on the cellulose molecule whereas other common reagents do not. These facts give rise to two general questions: first, what are the requirements for a reagent to have this specificity; and, second, are there any other reagents that would be expected to show an analogous behavior? Recently Heidt, Gladding, and Purves[114] have analyzed these questions and have postulated that there are four requirements necessary for the central atom of the oxidant in order to bring about such reactions. These properties are:

1. It must have a diameter of 2.5 to 3.0 A.
2. It must be able to coordinate at least two hydroxyl groups in addition to those groups already attached to it.
3. Its valence must be two units above the next lowest stable state.
4. It must have a standard oxidation potential of approximately -1.7 volts with respect to this next lower stable valence state.

On the basis of these reaction qualifications, these investigators predicted that both sodium perbismuthate ($NaBiO_3$) and the hydrated unstable trivalent silver ion (Ag^{+++}) should lead to the same type of oxidative cleavage as exhibited by periodate or lead tetraacetate since they possessed all four necessary properties. Their experiments on both soluble starch and ethylene glycol served to confirm these predictions. By the same token, since the common oxidants such as nitric acid, hypochlorite, dichromate, and permanganate lack one or more of the four necessary qualifications, they would not be expected to yield the dialdehyde type of structure.

This correlation between the organic chemistry of the oxidized celluloses and the inorganic and physical characteristics of oxidants has been of great value in that it provides a method by which predictions can be made of probable reaction courses. It is now possible by this analysis to state, without extensive laboratory investigation, whether or not a particular oxidizing reagent would be expected to form the dialdehyde type of oxidized cellulose. More correlations of this type undoubtedly will be made in the future, and these will eventually permit the prediction of the course of any cellulose oxidation.

The reaction mechanism postulated to clarify the alkaline cleavage of oxidized celluloses serves also to explain the much greater stability of periodate-oxidized celluloses which have undergone further oxidation so that the aldehyde groups are converted into carboxyls; thus:

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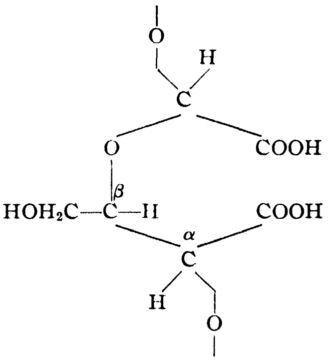
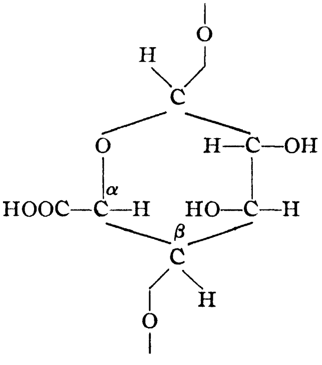
[114] L. J. Heidt, E. K. Gladding, and C. B. Purves, *Paper Trade J.*, **121**, 35 (Aug. 30, 1945).

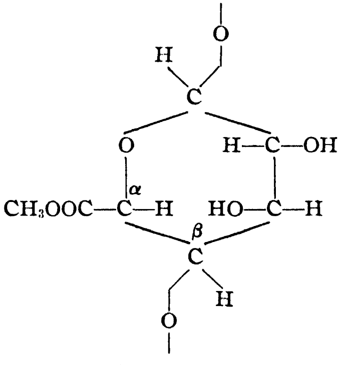


The carboxyl group will undergo ionization in an alkaline medium and become negatively charged. When this occurs the inductive effect of the group becomes reversed so that the hydrogen atom on the α-carbon is made much less acidic and cannot be readily removed by a base.

This conclusion has been confirmed by Vollmert[115] in his studies of the alkaline cleavage of pectic acid and its methyl ester. Pectic acid has the structure of a polyanhydrogalacturonic acid, one unit of which is shown in the accompanying sketch:



Pectic acid



Methyl pectate

Vollmert[115] showed that methyl pectate in alkaline solution undergoes a simultaneous de-esterification and depolymerization with the latter terminating when all of the ester groups have been hydrolyzed. This behavior would be expected since the ester group is strongly electronegative and would activate the hydrogen on the α-carbon as long as any ester linkage persisted in the molecule. Once de-esterification was complete, the ionized acid would no longer have this labilizing influence and depolymerization would cease.

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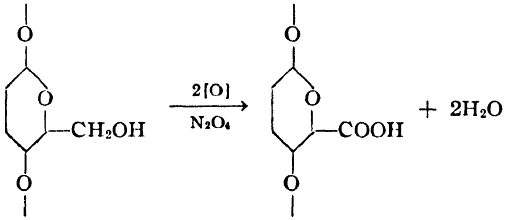
[115] B. Vollmert, *Makromol. Chem.*, **5**, 110 (1950).

The use of nitrogen dioxide (N_2O_4) for the preparation of oxidized cellulose has been investigated extensively by Kenyon and coworkers[116–124] and to a lesser degree by Maurer and Reiff[125] and Nevell.[126] These researches serve to show conclusively that the main reaction is the oxidation of the primary hydroxyl groups of the anhydroglucose units to the corresponding carboxyl groups as follows:



Early in these studies it was postulated that this oxidation was highly specific and that the only product was the polyanhydroglucuronic acid, one unit of which is depicted above. With the development of more information regarding the course of the oxidation and the properties of the products, it became apparent that these oxidized celluloses had many properties which could not be explained by the assumption of reaction specificity. These differences were observed mainly in cases which involved the reaction of alkalies with the oxidized cellulose. Such anomalies,

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[116] E. C. Yackel and W. O. Kenyon, *J. Am. Chem. Soc.*, **64**, 121 (1942).

[117] C. C. Unruh and W. O. Kenyon, *J. Am. Chem. Soc.*, **64**, 127 (1942).

[118] E. W. Taylor, W. F. Fowler, Jr., P. A. McGee, and W. O. Kenyon, *J. Am. Chem. Soc.*, **69**, 342 (1947).

[119] P. A. McGee, W. F. Fowler, Jr., and W. O. Kenyon, *J. Am. Chem. Soc.*, **69**, 347 (1947).

[120] C. C. Unruh, P. A. McGee, W. F. Fowler, Jr., and W. O. Kenyon, *J. Am. Chem. Soc.*, **69**, 349 (1947).

[121] P. A. McGee, W. F. Fowler, Jr., E. W. Taylor, C. C. Unruh, and W. O. Kenyon, *J. Am. Chem. Soc.*, **69**, 355 (1947).

[122] P. A. McGee, W. F. Fowler, Jr., C. C. Unruh, and W. O. Kenyon, *J. Am. Chem. Soc.*, **70**, 2700 (1948).

[123] E. C. Yackel and W. O. Kenyon (to Kodak Ltd.), Brit. Patent 531,283 (Jan. 1, 1941); *Chem. Abstracts*, **35**, 8294 (1941); (to Eastman Kodak Co.), U. S. Patent 2,232,-990 (Feb. 25, 1941); *Chem. Abstracts*, **35**, 3814 (1941).

[124] W. O. Kenyon and E. C. Yackel (to Eastman Kodak Co.), U. S. Patent 2,448,892 (Sept. 7, 1948); *Chem. Abstracts*, **43**, 404 (1949).

[125] K. Maurer and G. Reiff, *J. Makromol. Chem.*, **1**, 27 (1943).

[126] T. P. Nevell, *J. Textile Inst.*, **42**, T91 (1951).

when viewed in conjunction with those of oxidized celluloses obtained from the action of other oxidants, provided evidence that although the main reaction is that previously depicted, side reactions must occur which introduce aldehyde or ketone groups within the cellulose molecule.

The deviation of this oxidation from ideality can be observed by comparing the total acid content of the molecule, as measured by the calcium acetate method of Lüdtke,[127] with the uronic acid content measured by the method of Lefèvre and Tollens.[128] If there are no side reactions, the ratio of uronic acid (U) to total acid (A) should be one. The ratio determined experimentally showed an average value of 0.85 (mean deviation ±0.06) as illustrated in Table 11. The most direct evidence for side reactions lies in the fact that if every primary hydroxyl is oxidized to carboxyl, the product would have a carboxyl content of 568 millimoles per 100 g. of cellulose and would show a maximum oxygen consumption of 2 atoms per C_6 unit; actually, values of carboxyl have been observed as high as 700 millimoles per 100 g. of cellulose and oxygen consumptions as high as 2.7 atoms per C_6 unit.

TABLE 11

Comparison of Uronic Acid (U) to Total Acid (A) in N_2O_4-Oxidized Cellulose (Nevell[126])

Oxidized cellulose	Carboxyl content (millimoles/100 g.)	Ratio of U to A
1	23.5	1.07
2	84.9	0.90
3	132	0.81
4	181	0.86
5	216	0.85
6	323	0.77
7	488	0.77
8	537	0.78
9	546	0.83
10	691	0.83

The nature of the groups introduced into the cellulose molecule by side reactions during nitrogen dioxide (N_2O_4) oxidation have not been unequivocally proved. The evidence available at present indicates that both diketone groups in the 2,3- positions and aldehyde groups in the 6- position are formed. The presence of the diketone functional groups has been inferred[126] from the reversible color changes (yellow to colorless) that the oxidized cellulose will undergo on alternate drying and exposure to moisture. This color is similar to that of conjugated systems such as are present in glyoxal, diacetyl, or benzil, all of which are yellow in color. The colorless form of the oxidized cellulose could arise by hydration of the ketone which would destroy the conjugation as follows:

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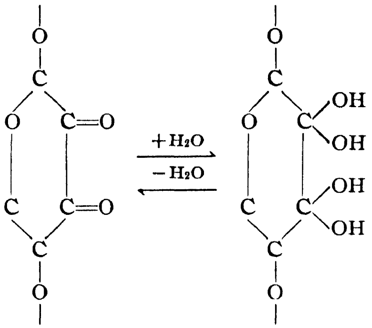
[127] M. Lüdtke, *Biochem. Z.*, **268,** 372 (1934).

[128] T. P. Nevell, *J. Textile Inst.*, **39,** T118 (1948).



(Yellow) (Colorless)

The reaction of chlorous acid on N_2O_4-oxidized cellulose increases the total acid content of the molecule, decreases the uronic acid content as well as the copper number, and reduces the alkali sensitivity of the oxidized cellulose. This behavior is characteristic of oxidized celluloses containing 2- and 3-aldehyde groups and thus points to their production during N_2O_4 oxidation.

(3) *Physical Nature of the Oxidative Reaction*

Thus far in the discussion of cellulose oxidation emphasis has been placed on the ability to separate oxidants into either specific or nonspecific reagents, and no mention has been made of the physical nature of their attack on cellulose. In actual practice, oxidation of cellulose fibers occurs in a heterogeneous fashion with the result that attack is not uniform in all portions of the fiber. The degree of nonuniformity during oxidation has been ably demonstrated by Hibbert and Parsons,[129] who made a thorough study of the action of permanganate salts and acetic acid solutions of chromic acid on cellulose. They observed that mixtures were produced composed of unattacked cellulose, some partially depolymerized cellulose, and other complex oxidation products showing acidic and aldehydic behavior.

In the majority of instances the heterogeneous reaction between cellulose and a reagent will occur by a rapid reaction in the disordered region of the

[129] H. Hibbert and J. L. Parsons, *J. Soc. Chem. Ind.*, **44**, T473 (1925); *Cellulosechemie* **7**, 97 (1926).

fiber, followed by either termination of the action or by a much slower reaction in the ordered region. In the case where action ceases with the disappearance of the disordered region, the x-ray diagram of the cellulose will remain unaltered during the degradation. If reaction is not limited to the readily available region but also can occur in the more highly organized portions of the fiber, a progressive change will be observed in which the x-ray patterns of the oxidized substance will differ from the original only in becoming more diffuse as the reaction proceeds.

Davidson[130] has investigated this effect with periodate- and chromic-oxidized cellulose, and Nevell[131] has extended it to nitrogen dioxide (N_2O_4) oxidations. Here again a marked difference has been observed between the more specific oxidants, periodate and nitrogen dioxide, and the nonspecific one, chromic acid. With the latter, oxidation does not result in any change in the x-ray diagram, and the effect is thus very similar to that observed during the acid degradation of cellulose. From these observations it is apparent that chromic acid is unable to penetrate and swell the crystalline areas of the fiber and thus its attack is limited to the amorphous region. With both of the specific types of oxidants, the reactions proceed throughout the entire structure of the molecule, and a gradual change in x-ray diagram is observed. This change is one of an increase in the diffuse nature of the characteristic cellulose bands but does not involve the introduction of any new bands. In this case the reagents appear to have the ability to swell the fiber, to penetrate into the crystalline region, and then to react in their normal fashion according to the organic chemistry of the process. This ability to swell and to penetrate is probably one of the most important features of the specific reagents and accounts to a fair extent for their ability to attack only certain points in the anhydroglucose unit. Nonspecific reagents, which are very powerful oxidants, are restricted physically in their reactivity and hence attack not only the amorphous region but will continue to react with the primary products of oxidation and produce a highly heterogeneous series of substances. The nature of the oxidation products will be different depending upon the concentration of the oxidizing reagent and the duration and temperature of the reaction. No oxidation is entirely free from this secondary oxidation effect, a factor which accounts for the production of some carbonyl functions in the N_2O_4-oxidized celluloses as well as some deviations from ideality which are observed with materials obtained from periodate oxidation.

Further substantiation of this concept of oxidation can be obtained from

[130] G. F. Davidson, *J. Textile Inst.*, **32,** T109 (1941).

[131] T. P. Nevell, *J. Textile Inst.*, **42,** T130 (1951).

the fact that at comparable degrees of oxidation both periodate- and N_2O_4-oxidized celluloses will retain their fibrous nature as well as a large proportion of their strength. Chromic-oxidized cellulose, on the other hand, has lost its fibrous structure and has been reduced to a friable powder. In the latter case, the amorphous region has been destroyed in the fiber with the resultant loss of strength due to excessive chain rupture, whereas the specific reagents have exerted their effect along the entire molecular chain and thus chain scission has been at a minimum.

It is this physical limitation imposed by the structure of the cellulose fiber which has made the production of distinct reproducible types of oxidized celluloses so difficult and has, to a large measure, been responsible for the contradiction and confusion which exist in the literature relative to oxidized celluloses.

(c) PROPERTIES OF OXIDIZED CELLULOSES

The discussions of oxidized celluloses in the previous sections have pointed out the chemical and physical heterogeneity of the reactions. It is to be expected therefore that the properties of oxidized celluloses would show a corresponding lack of uniformity, and would be a function of the oxidant employed and the conditions under which the reaction was conducted. Oxidized celluloses can vary in properties from being predominantly acidic to predominantly reducing with a complete spectrum of intermediate properties being possible. The major point of differentiation between the extremes lies in the ion-exchange properties of acidic oxidized celluloses (discussed below) and the alkaline lability of the reducing types (see topic (b) above and references 103–112).

(1) Ion-Exchange Properties of Acidic Oxidized Celluloses

The absorption of metals from solutions of their salts by oxidized celluloses was recognized as early as 1883 by Witz[132] as being an outstanding property of such materials. His observations can be explained today on the assumption of an exchange reaction between the cellulose carboxyls and the metallic ions as follows:[133]

$$R_{cell}COOH + [M]^+ \overset{HOH}{\rightleftharpoons} R_{cell}COOM + [H_3O]^+$$

The degree to which this equilibrium is displaced in either direction will depend upon the concentration of the hydronium ion and the metallic ion and to a considerable extent upon the nature of the metal ion M. Absorption will be favored and the equilibrium displaced to the right by a low concentration of hydronium ion and a high concentration of metallic ions. The ability of cations to bind cellulose carboxyls has been referred to as their "affinity"[134] for the cellulose carboxyls. A considerable variation in combining ability has been observed from ion to ion, an example of which is shown in Figure 26. In this illustration the amount of cation bound by hypobromite-oxidized cellulose has been related to the salt concentration in the aqueous solution; an approximately threefold difference is noted between the monovalent silver and tetramethylammonium ions at equal salt concentrations. It has been possible, from these investigations, to establish an increasing order of "affinity" which is: $N(CH_3)_4^+ < Li^+ < Na^+ < K^+ < Tl^+ < Ag^+ < Ca^{++}, Ba^{++}$ at a salt concentration of 0.01 *N*. At higher salt concentrations a similar order is observed except that the relative position of the silver and of the calcium and barium ions is interchanged.

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[132] G. Witz, *Bull. soc. ind. Rouen*, 11, 169 (1883).

[133] G. F. Davidson and T. P. Nevell, *J. Textile Inst.*, 39, T59 (1948).

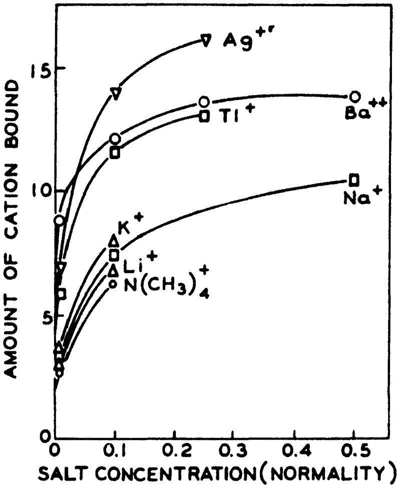

Fig. 26. Absorption of ions by oxidized cellulose from salt solutions at pH = 3.5 (Davidson[134]). The cation bound is recorded as milliequiv./100 g. oxidized cellulose.

The measured "affinity" of an ion for the carboxyl group of oxidized cellulose is composed of several factors. One of these is the relationship between exchanging power and ionic radius. In the case of the oxidized celluloses, the carboxyl groups are relatively fixed in position; therefore, for an ion to exchange, it must be able to reach the carboxyl group and to fit into a definite volume in space. As a result of this factor there is an inverse relationship between exchanging ability and ionic size; the smaller the ion is, the more completely will it be able to neutralize the cellulose carboxyls. Another size factor arises as a result of the electrical attraction between the cation and the anion which controls the retention of the cation by the carboxyl of the cellulose. The closer these two charges can approach one another, the greater is the force between them with attraction diminishing as the square of the distance between ion centers. An ion of large volume, because of its greater radius, will have its charge at a greater distance from that of the carboxyl group than will one of small volume, and the attractive force will be less. A highly hydrated ion, because of its large volume, likewise will be held less tightly than one which is less completely hydrated or not hydrated at all, and thus hydratability becomes another factor for consideration. A bivalent ion, because of its double charge, is even more tightly held in that it must be completely neutralized for electrical balance in the system. The behavior of bivalent ions is further complicated in that exchanges of ions of different valences will involve much greater activity coefficient differences than will occur between ions of the same charge type. The ratio between the activity coefficients of the bivalent ions and the monovalent hydrogen ion will therefore vary considerably with the ionic strength of the medium which in turn will affect the mass-action balance of the exchange. Certain ions, such as copper or lead, will be held more firmly because of their ability to form complexes with the hydroxyl groups as well as the carboxyl groups of the cellulose.

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[134] G. F. Davidson, *J. Textile Inst.*, **39**, T87 (1948).

On the basis of this discussion the relative order of "affinity" as determined by Davidson[134] is an understandable one. The position occupied by the large tetramethylammonium ion would be anticipated as a result of its size, charge distribution, and hydration; the alkali metals occupy positions which are direct functions of size and hydratability; silver will be held tenaciously in the same manner as it is held in AgCl; and the position of calcium and barium is a composite of both ionic strength effect and their double charge.

Acidic oxidized celluloses are inherently unstable if their carboxyl groups remain in the free acid form. This instability has been attributed by Davidson and Standing[135] to hydrogen-ion hydrolysis of glucosidic linkages in the cellulose molecule by the free cellulose carboxyls, and would account for the observed facts; namely, a rise in fluidity and copper number, and a decrease in carboxyl content of the undissolved oxidized celluloses. The magnitude of this effect is apparent from Table 12.

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[135] G. F. Davidson and H. A. Standing, *J. Textile Inst.*, **42**, T141 (1951).

TABLE 12

Effect of Various Treatments on Periodate-Chlorite Oxidized Celluloses (Davidson and Standing[135])

Temperature, 90°C.; Duration of Treatment, 24 hrs.

Conditions of treatment	Carboxyl content[a] (millimoles/100 g.)			Fluidity		Copper number	
	Initial	Final	% Fall	Initial	Final	Initial	Final
Water	6 85	4 06	41	12.5	34.1	0.15	0.98
0.2 *M* NaCl, pH 6.6	6.85	6.09	11	12 5	18.3	—	—
0.1 *N* NaOH	6 85	6.31	8	12 5	20.6	—	—
Water	13.7	7.7	44	17 7	42.5	0 39	1.45
0.2 *M* NaCl, pH 6.6	13.7	11 9	13	17 7	27 1	—	—
0.1 *N* NaOH	13.7	12.4	9	17 7	27.0	—	—

[a] By methylene blue method.

The decrease in carboxyl content can be explained by the assumption that hydrolysis of the glucosidic bonds would occur in rather close proximity to the carboxyl groups. This would result in the formation of fragments which were carboxyl-enriched, and such scission products would be of a size that would render them water-soluble; hence, the carboxyl content of the oxidized cellulose would show a corresponding decrease. This supposition received some verification in that, after treatment of a hypobromite-oxidized cellulose with distilled water at 90°C., the water showed a pH value of around 3.5. In another study, acidity measurements were made on the aqueous washings, and sufficient acidity was detected to account for the drop in carboxyl content observed with the oxidized cellulose.[135]

(2) *Hypohalite-Oxidized Celluloses*

Acidic oxidized celluloses are produced from cellulose by reactions with either alkaline hypochlorite or alkaline hypobromite.[87,90,136–138] The latter, however, is more satisfactory from the preparative viewpoint because of its much greater rate of reaction. These oxidations entail a loss of

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[136] G. F. Davidson, *J. Textile Inst.*, **43**, T291 (1952).

[137] C. Birtwell, D. A. Clibbens, A. Geake, and B. P. Ridge, *J. Textile Inst.*, **21**, T85 (1930).

[138] A. R. Urquhart, W. Bostock, and N. Eckersall, *J. Textile Inst.*, **23**, T135 (1932).

weight by the cellulose due to the formation of soluble oxidation products; this weight loss is small in the early stages of reaction but increases rather rapidly with oxygen consumption and approaches a value of 15% at an oxygen consumption of 0.4 atom per anhydroglucose unit.

The copper number of the hypobromite-oxidized cellulose increases at first and then becomes relatively constant with oxygen consumption, with a slight decrease being observed at high levels of oxidation. The fluidity increases with oxygen consumption but at a constantly decreasing rate, and at values above 0.25 atom per anhydroglucose unit the rate becomes very small and essentially linear. These observations are illustrated in Figure 27.

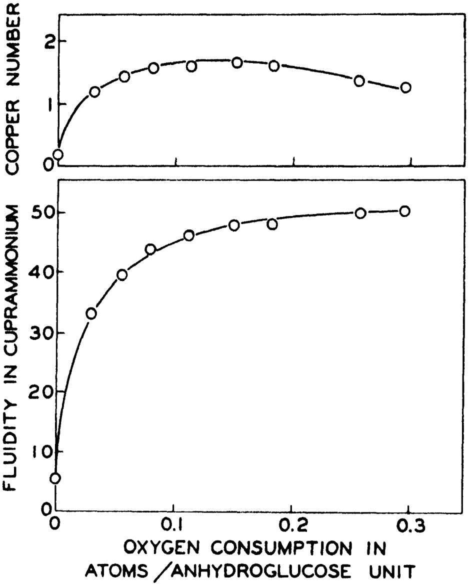

Fig. 27. Hypobromite-oxidized cellulose (Davidson[136]).

The tensile strength of the oxidized product falls progressively during oxidation; when oxygen consumption becomes greater than 0.2 atom per anhydroglucose unit, the original fiber has been reduced to a friable powder. At this point the hypobromite-oxidized cellulose shows no change in x-ray structure over that of the original cellulose; this is the same behavior as was observed with chromic-oxidized cellulose and is due to the physical heterogeneity of the oxidation.

The formation of carboxyl groups with progressive oxidation is illustrated in Figure 28. In the initial stages of oxidation (up to 0.05 atom of oxygen per anhydroglucose unit) the production of one carboxyl group requires an oxygen consumption of 3 atoms. This ratio increases as oxidation becomes progressively greater, and at 0.25 atom per anhydroglucose unit, 12 atoms of oxygen are required for the production of one carboxyl group in the oxidized cellulose.

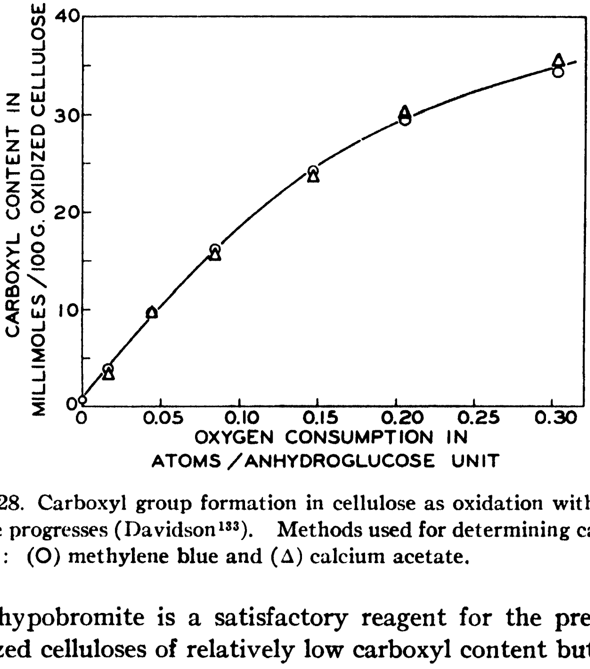

Fig. 28. Carboxyl group formation in cellulose as oxidation with hypobromite progresses (Davidson[133]). Methods used for determining carboxyl content: (O) methylene blue and (Δ) calcium acetate.

Alkaline hypobromite is a satisfactory reagent for the preparation of acidic oxidized celluloses of relatively low carboxyl content but is not preferred over nitrogen dioxide (N_2O_4) or the periodate-chlorous acid combination for the preparation of oxidized celluloses high in carboxyl content.

(3) *Nitrogen Dioxide-Oxidized Cellulose*[86,116–119,121,122,125,126,131]

The formation of acidic oxidized cellulose by the reaction of cellulose with nitrogen dioxide (N_2O_4) results in an increase in weight of the product rather than the decrease which was observed with the hypohalites. The observed increase is dependent upon the duration of the oxidation, the oxygen consumption, and the carboxyl content of the product. In Figure 29 are illustrated the results obtained for three series of oxidations carried out for 1-, 4-, and 10-day periods in which oxygen consumption is compared with weight increase. The broken line gives the theoretical relationship between weight increase and oxygen consumption which would exist if the only product of the reaction was the polyanhydroglucuronic acid resulting from oxidation at the 6- position. In all cases the experimental points fall below those calculated on the basis of the assumption of specificity.

The copper number of N_2O_4-oxidized cellulose shows a linear increase with carboxyl content and reaches a very high value which approaches 90 at a carboxyl content of 568 millimoles per 100 g. cellulose, corresponding to one carboxyl per anhydroglucose unit. The relative viscosity shows a rapid drop in the early stages of the reaction, decreasing from an initial value of 12.4 to a value of 1.5 at a carboxyl content of 100 millimoles per 100 g. Further changes in relative viscosity are minor so that at 250 millimoles per 100 g. the value has decreased only to 1.4.

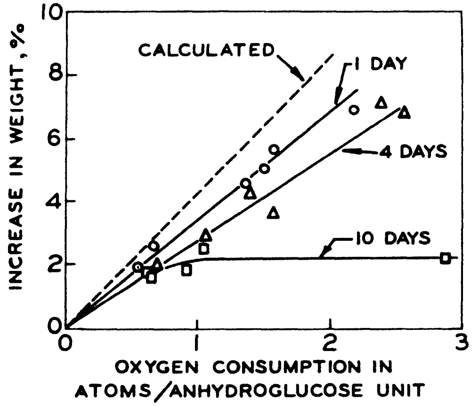

Fig. 29. N_2O_4-oxidized celluloses (Nevell[126]).

The relationship between tensile strength and carboxyl content of N_2O_4-oxidized cellulose is shown in Figure 30. The loss in strength is directly comparable to the change observed previously for the relative viscosity. In this case, despite the rather large decrease in strength, the oxidized cellulose retains its fibrous form. In contrast to the chromic- and hypohalite-oxidized celluloses, the N_2O_4 product shows a change in x-ray structure which indicates that the reaction is physically more homogeneous.

The carboxyl content of the N_2O_4-oxidized cellulose shows a linear increase with oxygen consumption, and, as previously noted, the carboxyl value can exceed the theoretical maximum for conversion of all the primary hydroxyl groups of the anhydroglucose units to carboxyls. The samples which have a high carboxyl content display an exceedingly high affinity for water and have moisture absorption ratios as high as 4. In this respect they differ from all other known types of acidic oxidized celluloses in that they alone show these high absorption ratios (see Chapters IV-D and XI).

Another distinguishing feature of N_2O_4-oxidized celluloses is the solvent action exerted upon them by nonalkaline aqueous solutions of electrolytes. Partial solution will result from the action of sodium bisulfite, sodium chlorite, veronal, and methylene blue on the oxidized celluloses.

Dilute sodium hydroxide (0.1 *N*) will completely dissolve N_2O_4-oxidized celluloses having carboxyl contents in excess of 200 millimoles per 100 g. of cellulose. Upon regeneration of the oxidized cellulose by acidification, however, only a fraction of this material can be recovered. For example, at a carboxyl level of 200 millimoles per 100 g. only 75% of the oxidized cellulose can be regenerated by acidifications, and at 700 millimoles per 100 g. only 10% can be recovered. This is striking evidence for the extensive degradation which is brought about by the alkali.

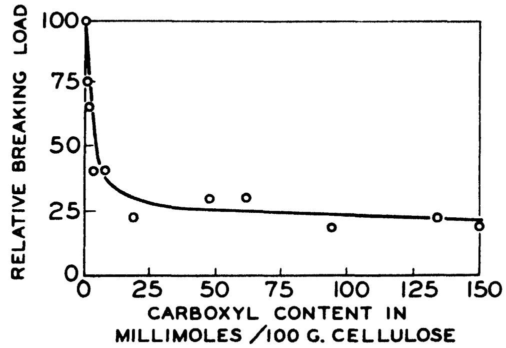

Fig. 30. Tensile strength of cotton yarn as oxidation with N_2O_4 progresses (Nevell[126]).

(4) *Reducing Type of Oxidized Celluloses (Periodic- and Chromic-Oxidized Celluloses)*[88,95,96,100,130,139]

The oxidation of cellulose by chromic or periodic acid yields products which are characterized in a general fashion by their high reducing power, low acidity, and extreme alkali sensitivity. The two oxidants differ however in their effects upon the specific properties of the oxidized celluloses;

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[139] E. L. Jackson and C. S. Hudson, *J. Am. Chem. Soc.*, **59**, 2049 (1937).

these properties include copper number, fluidity in cuprammonium, methylene blue absorption, and weight loss under standardized treatments with cold or hot dilute sodium hydroxide. In the case of the periodic-oxidized celluloses these properties show a continuous increase with the degree of oxidation, whereas with chromic-oxidized celluloses the increases are continuous until an oxygen consumption of 0.4 atom per anhydroglucose unit has been reached. With chromic-oxidized celluloses, at degrees of oxidation beyond this point, there is very little change in the values of the individual properties. In the early stages of reaction, the values of the periodic-oxidized celluloses, with the exception of methylene blue absorption, are much higher than those of the chromic-oxidized celluloses, and these differences become greater with increasing levels of oxidation.

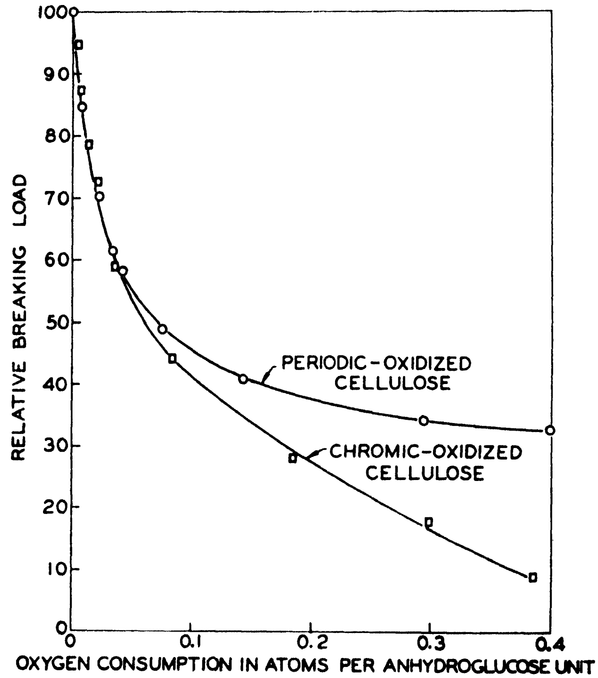

Fig. 31. Effect of oxidant on tensile strength of cotton yarn as reaction progresses. Data plotted are taken from Davidson.[140]

A marked dissimilarity is also observed in the tensile strength behavior of the two types of oxidized cellulose. In the early stages of the reaction, both show reductions in relative breaking strength which are essentially equivalent. After oxygen absorption of approximately 0.05 atom per anhydroglucose unit, the reduction in strength due to chromic acid becomes greater and continues at a relatively rapid rate for the duration of the oxidation. The change in tensile strength with the periodic acid oxidation slows down rapidly at this point and appears to be reaching a limiting value around 30% of the original. These differences are shown graphically in Figure 31.[140]

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[140] G. F. Davidson, *J. Textile Inst.*, 32, T126 (Table VII), T145 (Table VIII) (1941).

Both periodic- and chromic-oxidized celluloses show an increased hygroscopicity over the parent cotton. They differ in that the hygroscopicity of the periodic type shows a continuous increase with oxidation, whereas that of the chromic-oxidized type shows an initial increase and then becomes approximately constant at a moisture absorption ratio of 1.2. The periodic products reach the much higher level of moisture absorption ratio of about 1.8. In the case of the chromic-oxidized celluloses a portion of the increased hygroscopicity can be attributed to the chromium retention of the product, since a reduction in ash is accompanied by a reduction in moisture absorption ratio.

Treatment of sheeted cellulose with periodic acid results in pronounced shrinkage in area and a very marked swelling. Chromic acid, on the other hand, produces no changes of this type, and in this respect its action resembles closely that of hydrochloric acid.

The difference in properties of these reducing-type oxidized celluloses can be attributed to the physical nature of the attack of the oxidant. Periodic acid, as was discussed previously, has the ability to penetrate the ordered as well as the disordered regions of the cellulose fiber, whereas chromic acid attack appears to be largely confined to the disordered region. The continuous nature of the changes in the fluidity, copper number, and methylene blue absorption during periodic acid oxidation would be expected in the case where attack is not limited to any one area of the fiber. The pronounced swelling and increasing hygroscopicity are further confirmation of this postulation. The discontinuous change in chemical and physical properties as well as the negligible swelling and restricted hygroscopicity of chromic-oxidized celluloses result from a limited attack on the fiber. This discontinuous behavior is what would be predicted from the physical heterogeneity of the oxidative reaction.

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4. Degradative Effect of Light, Heat, and Laundering

L. F. McBurney

(a) EFFECT OF LIGHT

The degrading effect of light on cotton and linen fabrics has been realized for many years. Witz[141] in 1883 was the first investigator to demonstrate that the action of light was chemical in nature. Prior to his work, deterioration had been ascribed by Girard[142] to be due entirely to hydrolysis brought about by acidic materials in the atmosphere. Today it is known that the outdoor weathering of fabrics is the result of the combined effect of both photochemical and acidity factors as has been demonstrated by Race[143] (see Subsection C-1 of this Chapter III). The physical and chemical effects of degradation are a progressive loss in tensile strength of the fabric and a formation of carboxyl and carbonyl groups along the cellulose chain.[144–149] There are two general types of photochemical action which are responsible for cellulose degradation—photolysis and photosensitization.

(1) Photolysis

Photolysis brings about a direct scission of the chemical bonds and requires high-energy low-wavelength light. The direct degradation of cellulose involves the rupture of either carbon–carbon or carbon–oxygen bonds and has an energy requirement of the order of 80 to 90 kcal. per mole. Such a cleavage is possible with light of sufficiently low wavelength, e.g., the mercury resonance line of 2537 A. (10 Angstrom units = 1 millimicron).

Investigations have been made in this region of the far ultraviolet by various workers in which they have compared the rate of degradation in oxygen-containing and oxygen-free atmospheres.[149–158] It can be concluded from their studies that the degradation of cotton with radiation of

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[141] G. Witz, *Bull. soc. ind. Rouen*, **11**, 188 (1883).

[142] A. Girard, *Ann. chim. phys.*, [5], **24**, 337, 382 (1881).

[143] E. Race, *J. Soc. Dyers Colourists*, **65**, 56 (1949).

[144] G. Barr and I. H. Hadfield, *J. Textile Inst.*, **18**, T490 (1927).

[145] A. J. Turner, *J. Soc. Dyers Colourists*, **36**, 165 (1920).

[146] W. Scharwin and A. Pakschwer, *Z. angew. Chem.*, **40**, 1008 (1927).

[147] H. F. Launer and W. K. Wilson, *J. Research Natl. Bur. Standards*, **30**, 55 (1943).

[148] R. Haller and L. Wyszewianski, *Melliand Textilber.*, **17**, 325 (1936).

[149] P. W. Cunliffe and F. D. Farrow, *Shirley Inst. Mem.*, **7**, 1 (1928); *J. Textile Inst.*, **19**, T169 (1928).

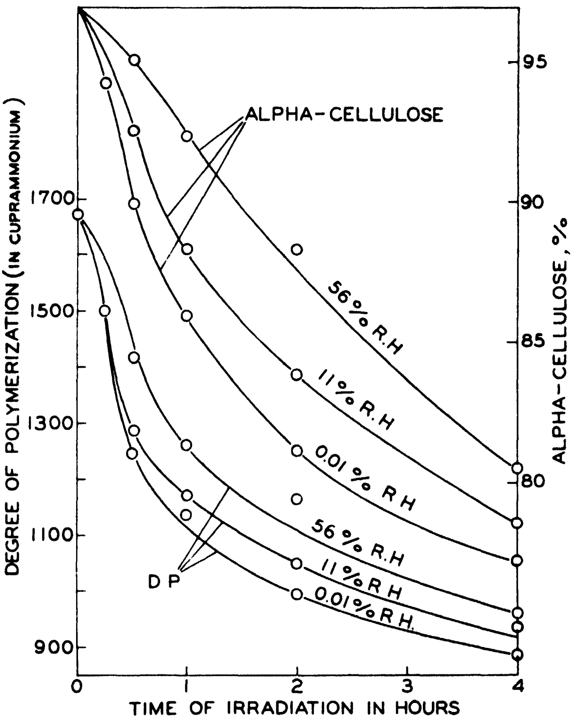

Fig. 32. Effect of water vapor (in per cent relative humidity (R.H.)) upon degradation of cotton cellulose (96.6% alpha-cellulose, D.P. 1660) during irradiation in the far ultraviolet region (Launer and Wilson[160]). The moisture content of the cellulose, calculated from typical desorption isotherms, at the three levels of humidity was 5.0, 2.0, and 0.002%.

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[150] Aston, *Reports and Memoranda* (*Advisory Committee for Aeronautics*), No. 396, Oct., 1917; through G. S. Egerton, *J. Soc. Dyers Colourists*, **63**, 161 (1947).

[151] S. Oguri and T. Yamaguchi, *J. Soc. Chem. Ind.*, *Japan*, **40**, Suppl. binding, 300B, 356B (1937).

[152] R. A. Stillings and R. J. Van Nostrand, *J. Am. Chem. Soc.*, **66**, 753 (1944).

[153] P. Waentig, *Z. angew. Chem.*, **36**, 357 (1923).

[154] P. Heermann and H. Sommer, *Leipzig. Monatschr. Textil-Ind.*, **40**, 161, 207 (1925).

[155] H. Kauffman, *Melliand Textilber.*, **7**, 617 (1926).

[156] G. S. Egerton, *J. Soc. Dyers Colourists*, **65**, 764 (1949).

[157] E. Heuser and G. N. Chamberlin, *J. Am. Chem. Soc.*, **68**, 79 (1946).

[158] G. S. Egerton, *J. Soc. Dyers Colourists*, **63**, 161 (1947).

[159] G. S. Egerton, *Textile Research J.*, **18**, 659 (1948).

wavelength 2537 A. is not dependent upon the presence of oxygen in the surrounding atmosphere. For example, in some cases (cotton and viscose rayon) the loss in strength in atmospheres of carbon dioxide, nitrogen, or helium was about the same as that in oxygen. A post-irradiation effect is also observed in the same three gases where cotton shows an increased deterioration after storage in the dark. The breakdown of cellulose, whether measured by loss in tensile strength, increase in fluidity, or increase in copper number, was observed to be greatly reduced under these conditions by the presence of vat dyes.[159] This desensitizing effect of vat dyes during irradiation by light of 2537 A. was obtained both in dry oxygen and atmospheric air. Similar deterioration occurred with dyed cotton in an inert atmosphere but to a lesser extent than with undyed cotton.

Water vapor was shown by Launer and Wilson[160] also to have an inhibitory effect upon the deterioration of cellulose brought about by ultraviolet light in the region of 2540 A. Their results are illustrated by Figure 32. The curves in this figure show that the effect of water vapor persists until the cellulose has undergone considerable degradation (alpha-cellulose = 85%; degree of polymerization (D.P.) = 1150). From this point on, the curves tend either to approach each other or become parallel, thus indicating a termination of the inhibition.

Photolysis, although possible with cellulose as has been shown in this brief review, is of minor importance since wavelengths of light are required which are seldom realized in actual usage.

(2) *Photosensitization*

Despite the fact that cellulose and most of its derivatives are quite transparent in the visible and near-ultraviolet region, it is frequently observed that degradation will occur on exposure to ordinary light. In such systems where the reactant is incapable of absorption of the incident light to any major extent, a chemical change will occur only if another substance is present which is capable of absorbing the light and conveying the resultant energy to the reacting molecules. When such an energy transfer occurs and the absorbing medium is not itself permanently transformed, the process is called photosensitization.

This behavior in the case of textile materials is associated with three major factors: sensitizers, oxygen, and moisture. A variety of dyes and of pigments such as zinc oxide and titanium dioxide are capable of absorbing in the visible or near-ultraviolet region and making the resulting energy available for the degradation of the cellulose fiber. The effectiveness of certain dyes as sensitizers can be appreciated by examining the "degradation spectrograms" taken from the work of Lanigan[161] and shown in Figure 33. These photometric traces of spectrograms were obtained by the irradiation of cellulose with the mercury spectrum, moist air acting as the only oxidizing reagent. In the case of the undyed samples, rather poorly defined peaks were obtained in the ultraviolet regions of the spectrum at wavelengths of 3650 A. and lower, but none at the longer wavelengths in the visible portion of the spectrum. On the other hand, the dyed samples

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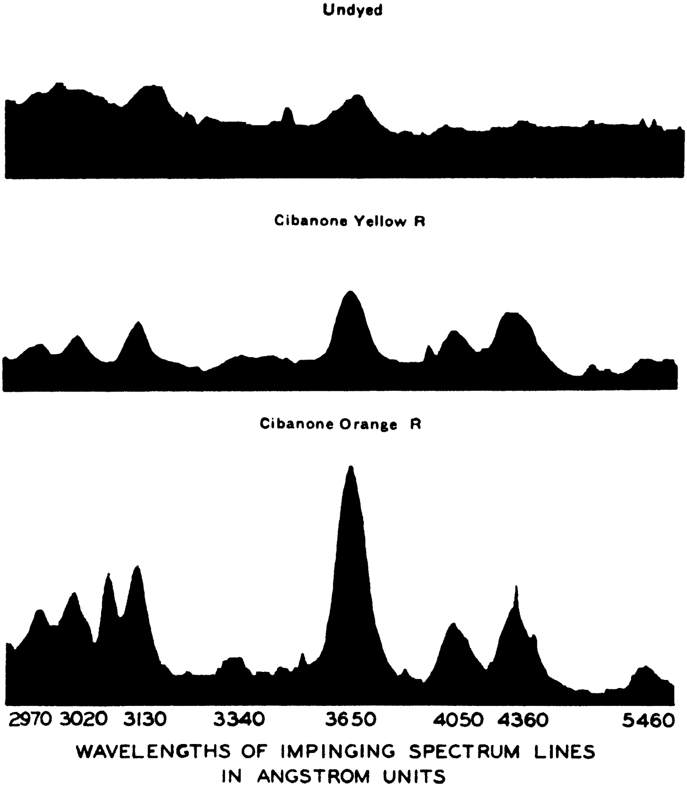
[160] H. F. Launer and W. K. Wilson, *J. Am. Chem. Soc.*, 71, 958 (1949).


Undyed

Cibanone Yellow R

Cibanone Orange R

Fig. 33. Microphotometric traces of degradation spectrograms of viscose sheets obtained in presence of moist air (Lanigan[161]).

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[161] H. Lanigan, *J. Textile Inst.*, **39**, T285 (1948).

showed not only an increase in the definition of the trace in the ultraviolet but also the development of well-defined peaks at the longer wavelengths such as 4050, 4350, and 5460 A.

The photosensitized deterioration of cellulose is in marked contrast to the photolytic reaction which occurs with radiation of 2537 A. in that it has been conclusively shown[158, 159, 162, 163] that oxygen is required for degradation and that the dyes act as initiators of the reaction rather than as inhibitors.

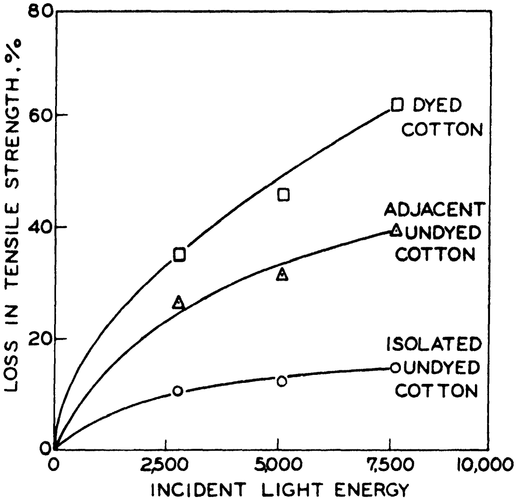

Fig. 34. Undyed yarns and yarns dyed with Cibanone Orange R exposed to sunlight in air at 100% relative humidity (Egerton[159]). The incident light energy is expressed in microwatt-hrs./sq. cm./10 A. at a wavelength of 4600 A.

The photochemical activity of the vat dyes toward promoting the oxidation of cellulose is largely confined to the yellow, orange, red, and a few brown members of the group. This same general statement of relative reactivity applies equally well to the sulfur and basic dyes.[164] Attempts have been made to relate the structure of dyes to their ability to promote tendering of cotton fibers. The work of Landolt[165] has been especially notable in this respect, but from his results it is unlikely that any general rule can be devised for tendering based on chemical constitution.

[162] G. S. Egerton, *J. Textile Inst.*, **39**, T293 (1948).

[163] G. S. Egerton, *J. Soc. Dyers Colourists*, **64**, 336 (1948).

[164] D. Ashton, D. Clibbens, and M. E. Probert, *J. Soc. Dyers Colourists*, **65**, 650 (1949).

[165] A. Landolt, *J. Soc. Dyers Colourists*, **65**, 659 (1949).

Moisture was shown by Egerton[158,159,163] to enhance the photosensitized degradation of cellulose. In this instance the presence of water vapor not only enhances the degradation of the dyed fabric but is also capable of catalyzing the breakdown of adjacent undyed fibers. This "action at a distance" is illustrated by Figure 34. The curves in this figure show that moisture will accelerate the rate of deterioration of an undyed sample which is adjacent to a dyed fiber so that its rate becomes intermediate between that of the isolated undyed and dyed cotton. The action of the dyed thread on the adjacent undyed one is almost independent of the distance between them over the range of 0.3 to 8 mm. When several undyed threads are interposed between successive dyed ones however, the effect is almost entirely confined to those nearest the dyed material. A similar behavior is observed when either zinc oxide or titanium dioxide is employed as the sensitizing reagent.

A difference in moisture activation has been observed between cotton and viscose rayon[159] which is unexpected since both materials appear to degrade by the same photosensitized oxidation. Viscose rayon shows a greatly reduced degree of deterioration in comparison to cotton. For example, cotton at 0 and 100% relative humidity shows a tensile loss of 23 and 42% respectively. Viscose rayon, on the other hand, under the same conditions shows a constant 17% loss.

The effect of moisture in these reactions can be attributed to the production of hydrogen peroxide by the photochemical oxidation of water sensitized by the presence of either a dye or an active pigment. The photochemical degradation of the dyed cotton can then be attributed to the combined effect of a direct oxidation of cellulose by air and an indirect oxidation due to the hydrogen peroxide. This mechanism gives a satisfactory explanation of the accelerating effect of humidity on the rate of deterioration of cotton as well as explaining the "action at a distance" effect of dyed fibers on undyed fibers.

Several techniques have been found serviceable to retard this photosensitized degradation. Sometimes an inactive dye protects the fabric in the presence of an active one, but this can ordinarily be taken advantage of only in shades requiring some blue or green component. Most interesting from the point of view of cellulose chemistry as a whole is the behavior of certain metal ions.

It has been found empirically that certain fugitive colors can be stabilized by the presence of minute amounts of copper.[164] Interestingly enough, not only is the dye protected from fading but the fabric is protected from oxidative tendering. This behavior of copper is carried over to an extent to the more stable vat dyes. Here it is found that about 40 parts per million of copper is sufficient to dominate completely the oxidation of the cellulose. The rate of oxidation does not depend on the nature of the dye, and is intermediate between undyed fabric and that dyed with an active dye. It appears from the work reported to date that optimum protection of the fabric occurs if it is treated with a solution containing enough copper to exchange with all acid groups of the dyed fabric and is then washed free of excess copper.

A clue to the action of copper may be found in the fact that it, as well as iron and cobalt, can completely prevent the evolution of hydrogen peroxide from a dyed fabric exposed to light and moisture. Manganese has somewhat the same action, chromium less, and nickel none at all. It is probable that these metals interact with the photoactivated dye molecule before the latter can extract a hydrogen from the organic environment.

In general, the more stable dyes are very similar in action to the colored metal ions noted for their promoting effect on oxidation. The dyes as well as the metal ions can absorb the high-energy radiation in the blue to near-ultraviolet region, can make this energy available for chemical reaction, and can change effective valence by one unit at a time. This valence change is reversible. The leuco (i.e., reduced) form of the dye and the lower valence state of the metal can interact with hydrogen peroxide or hypochlorous acid to give free radicals. As a result, cellulose treated with bleaching agents in the presence of the leuco dyes or the metal ions is severely degraded. The inhibition of these degradations seems to depend on the same characteristics that are effective in other oxidizing systems.

(b) EFFECT OF HEAT

Cellulose is relatively unaffected by normal drying conditions when the temperature is moderate and the time of exposure is not unduly prolonged.

TABLE 13

Effect of Oxygen and Moisture in Sealed-Tube Aging of Viscose Tire-Cord Yarn (Waller, Bass, and Roseveare[180])

Aging conditions	Heat-aging loss, %[a]
Dry yarn in nitrogen atmosphere	4
Moist yarn[b] in nitrogen atmosphere	6
Dry yarn in atmosphere of dry air	5
Moist yarn in atmosphere of air	55

[a] Per cent loss in oven-dry breaking load of yarn after heating 4 hrs. at 150°C.

[b] Yarn sealed in tube at 12% moisture regain.

In fact, cellulose can be heated at temperatures up to 140°C., and if the duration of treatment is kept below 4 hrs.[166] with a low initial moisture content, very little change will occur. Above 140°C. cellulose undergoes both chemical and physical modifications which take the form of a development of carbonyl and carboxyl groups and an increase in fluidity.[167–176]

The degree to which this degradation occurs is dependent upon variables other than simple time–temperature relationships. Included in these secondary factors are the nature of the cellulose (native or regenerated) undergoing treatment, the presence of air and/or moisture, and whether or not the samples are allowed to remain in contact with the products of decomposition.

The effect of drying conditions on the properties of textile yarn was studied by Wiegerink.[177] He observed that deterioration occurred either as the temperature was elevated or as the moisture content of the surrounding atmosphere was increased. Subsequent to this investigation, a number of studies have been made on cotton and rayon tire cord which have served to clarify the effect of moisture as well as air on this degradation.[178–182]

It has been clearly demonstrated that air and moisture have a synergistic effect on the degradation of cellulose. The extent of this behavior can better be appreciated by reference to Table 13.

The results of such investigations seem to indicate an oxidative mechanism for the heat degradation of cellulose. The primary product of thermal deterioration would be an oxycellulose, with this initial product undergoing a subsequent decomposition on prolonged heating. Moisture serves to accelerate the consumption of oxygen, thus explaining the synergistic effect

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[166] C. Dorée, *The Methods of Cellulose Chemistry*, 2d ed., Chapman & Hall, London, 1950, p. 216.

[167] E. Knecht, *J. Soc. Dyers Colourists*, **36**, 195 (1920).

[168] H. Fletcher and M. H. Houston, *Textile Research*, **11**, 4 (1940).

[169] S. Oguri and M. Takei, *J. Soc. Chem. Ind., Japan*, **41**, Suppl. binding, 3 (1938).

[170] H. Staudinger and J. Jurisch, *Papier-Fabr.*, **37**, Tech.-wiss. Tl., 181 (1939).

[171] H. Staudinger and E. Dreher, *Ber.*, **69B**, 1091 (1936).

[172] K. Götze and A. Reiff, *Zellwolle, Kunstseide, Siede*, **45**, 368 (1940).

[173] M. H. Houston and H. Fletcher, *Trans. Kansas Acad. Sci.*, **43**, 309 (1940); *Chem. Abstracts*, **35**, 2330 (1941).

[174] Z. A. Rogovin, V. A. Kargin, and V. Smirnov, *Tekstil. Prom.*, **1941**, No. 3, 40; *Chem. Abstracts*, **37**, 6134 (1943).

[175] E. Glücklich, *Textil-Ring*, **1**, 29 (Sept., 1943); *Chem. Abstracts*, **40**, 5925 (1946).

[176] K. Kanamaru, *J. Soc. Chem. Ind., Japan*, **46**, 1277 (1943)

[177] J. G. Wiegerink, *J. Research Natl. Bur. Standards*, **25**, 435 (1940).

[178] J. H. Dillon and I. B. Prettyman, *J. Applied Phys.*, **16**, 159 (1945).

[179] C. M. Conrad, W. J. Lyons, and V. W. Tripp, *Textile Research J.*, **16**, 324 (1946).

[180] R. C. Waller, K. C. Bass, and W. E. Roseveare, *Ind. Eng. Chem.*, **40**, 138 (1948).

[181] C. M. Conrad, V. W. Tripp, and T. Mares, *Textile Research J.*, **21**, 726 (1951).

[182] V. W. Tripp, T. Mares, and C. M. Conrad, *Textile Research J.*, **21**, 840 (1951).

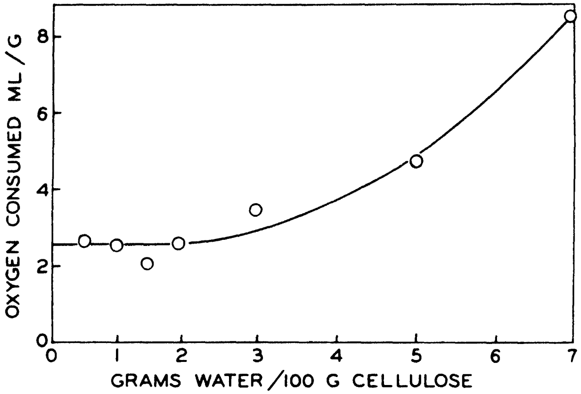

Fig. 35 Effect of water on the absorption of oxygen by viscose tire-cord yarn at 170°C. (Waller, Bass, and Roseveare[180])

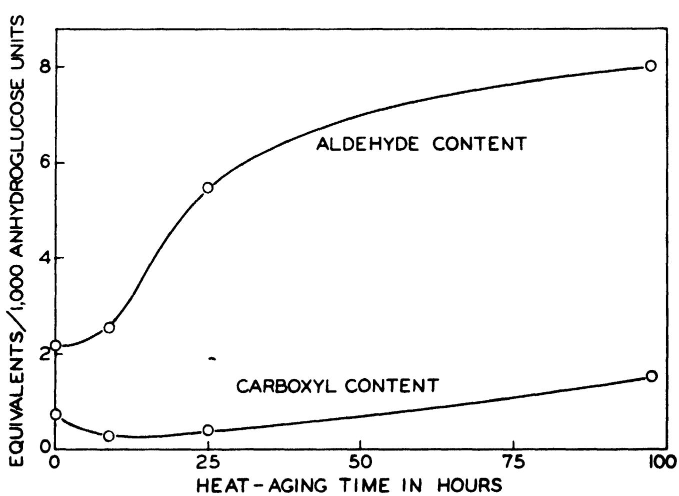

Fig. 36. Development of functional groups during heat degradation of dry viscose tire-cord yarn in air at 150°C. (Waller, Bass, and Roseveare[180]).

on the over-all reaction. The catalytic behavior of water vapor is illustrated in Figure 35 where it can be seen that moisture content of 2% or more has a marked accelerating effect on the rate of oxygen absorption.

As degradation proceeds, both aldehyde and carboxyl groups develop as shown in Figure 36. The minimum in the carboxyl curve can be ascribed to the thermal decomposition of carboxyl groups originally present in the cotton yarn, which leads to the evolution of carbon dioxide. Physical changes which accompany these chemical modifications include a reduction in moisture-regain capacity and a loss in yarn strength.

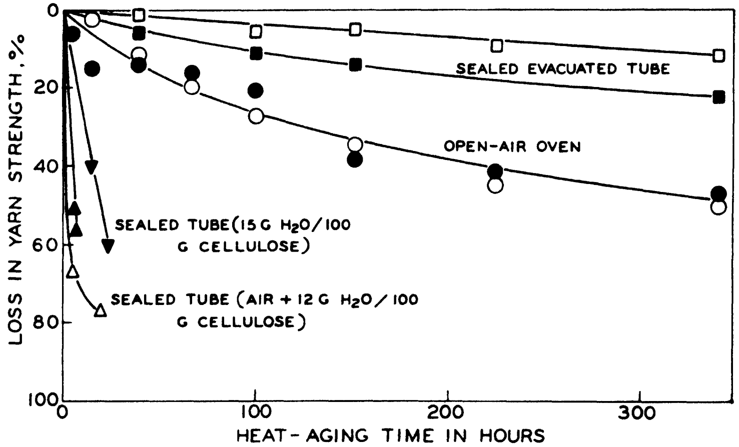

Fig. 37. Effect of oxygen and water on the tensile strength of viscose tire-cord yarn at 150°C. (Waller, Bass, and Roseveare[180]). The two different yarn samples tested are distinguished on the curves by open and closed symbols

The effect of the products of decomposition upon the rate of loss of yarn strength is illustrated in Figure 37. The combined effect of moisture, air, and degradation products in sealed tubes, produces as great a loss in 1 hr. as occurs in 40 hrs. of oven-aging or 200 hrs. of aging in sealed evacuated tubes. The loss in yarn strength is not uniform with time but appears to go through three distinct phases. They are an induction period, an interval of rapid degradation, and finally a phase of rather slow aging. The induction period is a result of the catalytic behavior of the decomposition product carbon dioxide, and can be shortened or prolonged by the absence or presence of absorbants such as amines or basic salts.

Loss in yarn strength tends to level off after a period of aging in the presence of air and moisture. The position of this plateau appears to be a function of aging conditions. This behavior is illustrated in Figure 38 where it is shown that a change in the moisture content from 2 (curve 1) to 12 g.

(curve 2) per 100 g. of cellulose changes the leveling-off point from 25 to 60% loss of tensile strength, and a further increase in water to 22 g. (curve 3) per 100 g. of cellulose results in a total loss of strength.

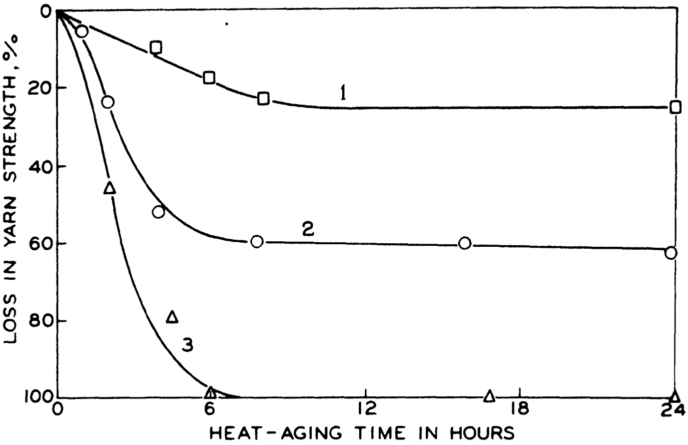

Fig. 38. Effect of moisture content on the tensile strength of viscose tire-cord yarn during aging at 150°C. in sealed tubes containing air (Waller, Bass, and Roseveare[180]). Curves 1, 2, and 3 represent, respectively, samples with 2 g., 12 g., and 22 g. of water per 100 g of cellulose.

The difference in behavior of cotton and rayon, when exposed to high temperature in laboratory aging tests, is illustrated in Table 14. Cotton cord degrades much more rapidly than rayon in the absence of air and moisture, but this order is reversed in the presence of 2% moisture and air, with rayon showing a greater loss in strength.

TABLE 14

Percentage Loss in Oven-Dry Strength of Cotton and Rayon Tire Cords on Heat-Aging (Waller, Bass, and Roseveare[180])

Aging time, hrs.	Continuous vacuum, 170°C.		Sealed evacuated tubes, 170°C.		Air and moisture (2%), 150°C.	
	Cotton	Rayon	Cotton	Rayon	Cotton	Rayon
4	—	—	—	—	4	9
8	—	—	—	—	11	39
16	—	—	—	—	23	46
24	14	4	21	10	41	100
48	21	7	43	20	—	—
72	29	6	67	30	—	—
96	31	9	—	—	—	—

From these data it is apparent that heat degradation of cellulose below pyrolytic temperatures is mainly oxidative with rather minor losses in strength being observed in the absence of oxygen and moisture. At extremely high temperatures a drastic decomposition will result with the production of carbon dioxide, carbon monoxide, water, β-glucosan, and minor amounts of hydrocarbons such as methane and ethylene.

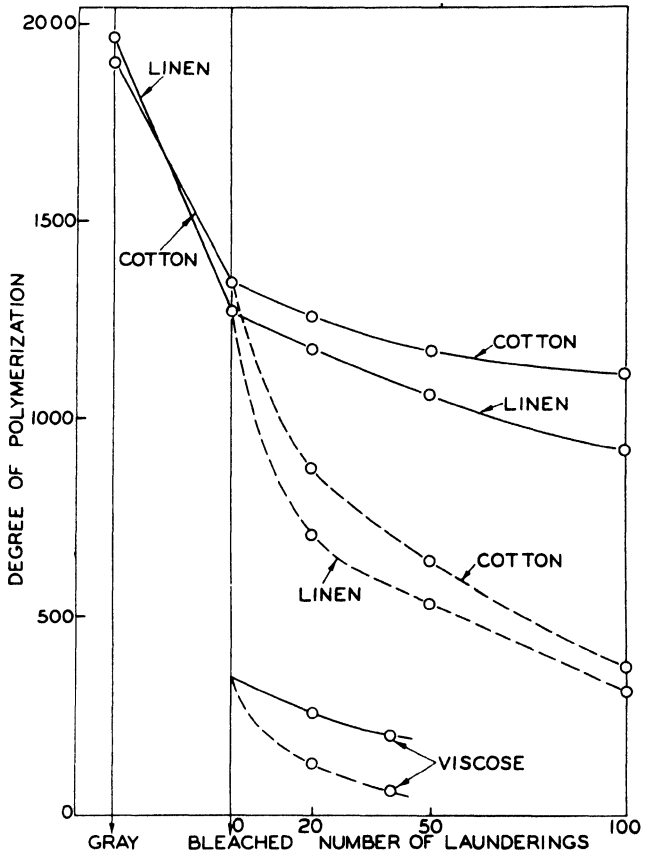

Fig. 39. Degree of polymerization of cellulose of fabrics in gray and bleached states and after laundering (Honegger and Schnyder[187]). Washing liquor: —— soft water and soap; – – – soft water, soap, and perborate. See text p. 180.

The alkali-soluble fraction of a heat-degraded cellulose has been termed "pyrocellulose."[183,184] This material resembles an oxidized cellulose in that it will reduce Fehling solution and shows an increased carboxyl content as evidenced by methylene blue absorption.

(c) EFFECT OF LAUNDERING

The changes which occur in cotton fabrics during wearing are not too well understood; however, it is generally realized that the major source of degradation results from the washing process rather than service wear. During laundering two types of deterioration can occur; one is due to mechanical damage produced by abrasion,[185,186] and the other is a chemical change brought about by the washing conditions. The chief source of the chemical damage appears to be in the bleaching[187] operation as can be seen by reference to Figure 39. The points on the extreme left represent unbleached cotton fabrics. When these fabrics are laundered with soft water, soap, and soda ash (Na_2CO_3), a slow reduction in degree of poly-

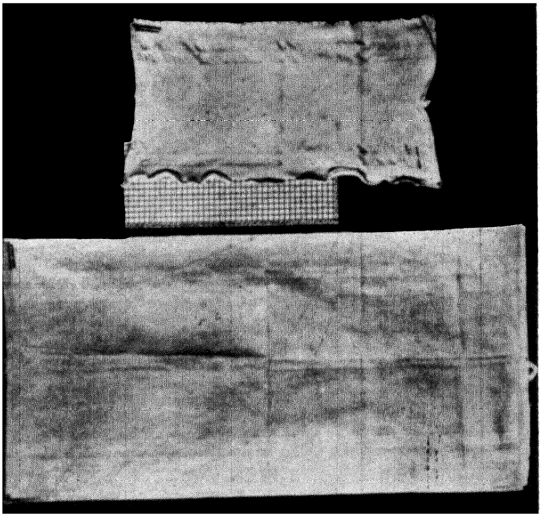

Fig. 40. Excessive shrinkage, after repeated washings, of a towel made from viscose staple (Reumuth[188]).

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[183] N. Kozhin, *Baumwoll-Ind.*, **6**, No. 3, 29 (1936); *Chem. Zentr.*, **1938, I**, 2096.

[184] E. Steurer and K. Hess, *Z. physik. Chem.*, **193**, 253 (1944).

[185] E. Walter, *Kunstseide u. Zellwolle*, **21**, 402 (1939).

[186] K. Schönleber, *Melliand Textilber.*, **21**, 228 (1940).

[187] E. Honegger and A. Schnyder, *J. Textile Inst.*, **34**, T29 (1943).

merization (D.P.) is observed. The addition of a bleaching agent, sodium perborate in this case, results in a rapid depolymerization, and after 100 washings the average D.P. has fallen to 400.

Major changes of a similar magnitude are observed with viscose fabrics when they are subjected to bleaching conditions.

Even colored cotton fabrics that are not bleached show considerable damage in laundering. This damage may vary widely from excessive shrinkage coupled with rapid loss of strength to moderate shrinkage and good strength after repeated washing. The portion of damage due to the actual washing process, and not to degradation resulting from ironing and exposure to light during drying and service, can be studied by microscopic examination of the fiber.[188]

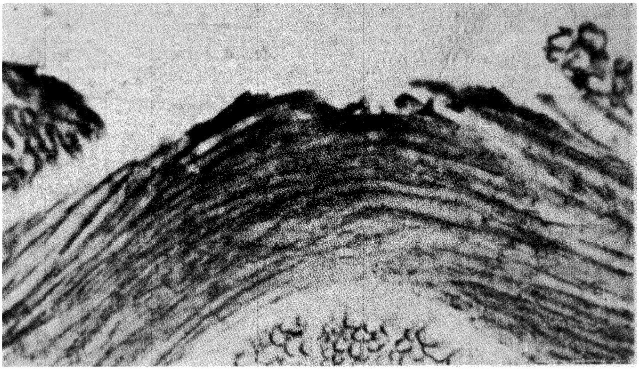

Fig. 41. Damage of cotton fabric caused by deposition of incrustants (Reumuth[188]).

Figure 40 shows an example of excessive shrinkage of a towel made from viscose staple. The individual fibers, originally smooth, have undergone fibrillation and are worn in two after repeated washings. This effect is most pronounced in the high spots of the fabric. Such damage to a fiber can be predisposed by a high content of low-D.P. cellulose in the sample.

The deposition or loading of either cotton or viscose fabrics with incrustants from hard water and soap have been shown to be injurious to the cellulose[189] (Fig. 41). These deposits appear to occur at points of incipient damage and result in an embrittlement of the fiber which causes a rapid failure. The deposition of calcium and magnesium compounds during laundering with hard water increases very rapidly with the first 50 washes as is shown in Figure 42. This behavior has been demonstrated to occur not only during the washing cycle but also during the rinses. Thus a considerable increase in fabric durability can be realized by using soft water during both washing and rinsing.

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[188] H. Reumuth, *Kunstseide u. Zellwolle*, **28**, 194 (1950).

[189] O. Oldenroth, *Bastfaser*, **3**, 10 (1943); *Chem. Abstracts*, **38**, 1373 (1944).

From an examination of a summary of the methods for detecting laundering damage[190] and from subsequent publications,[191–193] it is apparent that methods which measure the change in D.P. show the best correlation with actual usage. By utilizing such measurements, it has been possible to show that for maximum service the increase in fluidity should not exceed 3.5 rhes for 20 washes. Another valuable tool has been the Congo red staining test of Clegg.[194] In this test a fiber is swollen in sodium hydroxide and then

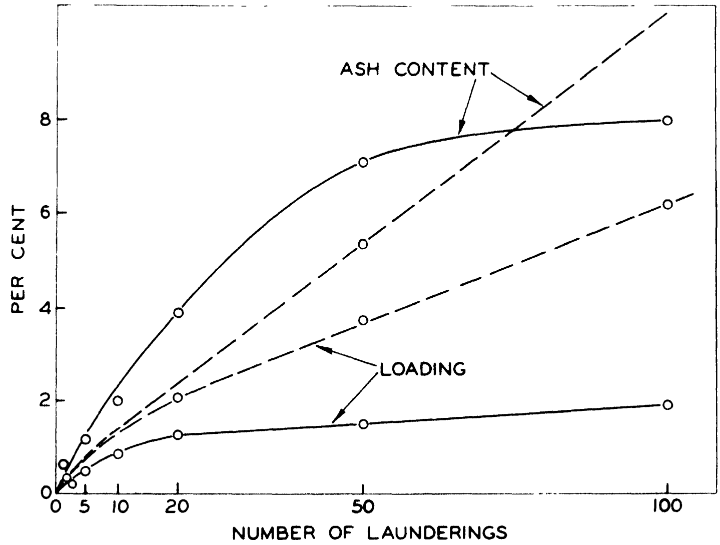

Fig. 42. Effect of laundering on percentage of ash content and of loading of calcium and magnesium compounds; cotton fabric (Honegger and Schnyder[187]). Washing liquor: —— hard water and soap; ---- hard water and combination detergent consisting of 1 part of sulfated fatty alcohol and 2 parts of a fatty acid condensate.

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[190] *Cowles Technical Tips*, **3**, Nos. 6 and 7 (1935).

[191] R. B. Smith, *Starchroom Laundry J.*, **45**, No. 9, 38, 42 (1938).

[192] M. E. Murdison and J. S. Roberts, *J. Textile Inst.*, **40**, T505 (1949).

[193] A. C. van Vreeswijk, *Chem. Weekblad*, **38**, 598, 618 (1941).

[194] G. G. Clegg, *J. Textile Inst.*, **31**, T49 (1940).

stirred with Congo red. If, according to Clegg, the primary wall has been undamaged, the entire fiber becomes a uniform pink. In the event of primary wall rupture or damage, the secondary wall of cellulose is exposed and is stained a bright red, thus highlighting any areas of deterioration.

The commercial laundry can utilize the principles discussed in this brief review to improve the life of cotton fabrics. The average home laundry however would find it impossible to control closely the pH, water softness, and other factors. For this reason, a wide field of research is available with its object the development of safe efficient bleaches for home utilization.

5. Microbiological Degradation

R. G. H. SIU

Cellulose is being degraded continually in nature by hundreds of species of fungi, bacteria, and actinomycetes.[195,196] This process of decomposition has tremendous natural significance as well as important economic considerations. Its role in the perpetuation of the vital carbon cycle is one of the decisive processes sustaining over-all life as we know it. On the undesirable side of the ledger, however, the annual damage to materials as a result of this decay runs into several billions of dollars. These implications have stimulated considerable investigative activity.[197] The focal point of more recent basic studies in this field has been a clarification of the complex mechanism of decomposition. Our present state of understanding on this mechanism is summarized in the subsequent paragraphs. Since most of this work has been carried out on cotton, it will be used as the reference substrate.

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[195] P. B. Marsh, K. Bollenbacher, M. L. Butler, and K. B. Raper, *Textile Research J.*, **19**, 462 (1949).

[196] E. T. Reese, H. S. Levinson, M. H. Downing, and W. L. White, *Farlowia*, **4**, 45 (1950).

[197] For complete monographic treatment including identity, physiology, and biochemistry of cellulolytic organisms, and methods of mildewproofing cotton fabrics see R. G H. Siu, *Microbial Decomposition of Cellulose*, Reinhold, New York, 1951. For wood see G. M. Hunt and G. A. Garratt, *Wood Preservation*, McGraw-Hill, New York, 1938; W. P. K. Findlay, *Decay of Timber and Its Prevention*, H. M. Stationery Office, London, 1946; J. S. Boyce, *Forest Pathology*, 2d ed., McGraw-Hill, New York, 1948.

(a) SUCCESSIVE HISTOLOGICAL CHANGES

The first change noticed in the decomposition of raw cotton fiber is a dissolution of the primary wall which is largely noncellulosic. One way to demonstrate this is by observations[198–200] on fibers swollen with alkali and carbon bisulfide. In the case of undegraded fibers, there occurs a ballooning effect. The swelling agents act on the secondary cellulosic wall, but the primary wall remains unswollen. Expansion of the secondary wall results in a bursting of the primary wall, pieces of which slip together as restrictive bands. The beaded structure is therefore indicative of the presence of the primary wall. The picture is quite different in microbiologically degraded fibers. As shown in Figure 43, no beading occurs. In the absence of the primary wall, the secondary cellulosic wall expands uniformly, and a straight fiber outline results. (See also Chapter IV-C.)

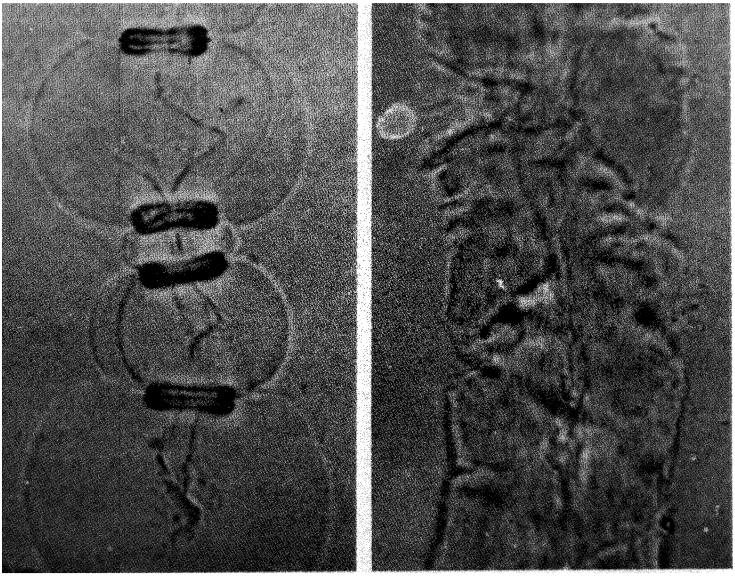

Fig. 43. Removal of primary wall by bacteria. Fibers swollen with alkali and carbon bisulfide. Left, undegraded; right, degraded for 4 days (Hooper[198]). Courtesy of Boyce Thompson Institute.

Whereas the dissolution of the primary wall seems to be a generalized affair, there is evidence[201-204] to suggest that the secondary cellulosic wall is attacked in a localized manner at the point of contact with the organism. In the case of the fungi, the decomposition appears to be centered around the filament tips. This is not unexpected inasmuch as these tips are the most actively growing portion of the fungus. The wall of the fungus is also thin at the tips, permitting the greatest amount of exchange with the environment. Proceeding in this fashion, the threadlike hypha pierces the secondary wall. There is no explanation, however, for the direct penetration at a right angle to the fiber axis. Within the lumen, the fungus continues to grow. The fiber is digested from the inside outwards. A photomicrograph of a fungal-digested fiber is shown in Figure 44. The etched-out areas are clearly visible.

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[198] F. E. Hooper, *Contribs. Boyce Thompson Inst.*, **10**, 267 (1939).

[199] A. C. Thaysen and H. J. Bunker, *J. Roy. Microscop. Soc.*, **21**, 303 (1923).

[200] R. K. Zuck and W. W. Diehl, *Am. J. Botany*, **33**, 374 (1946).

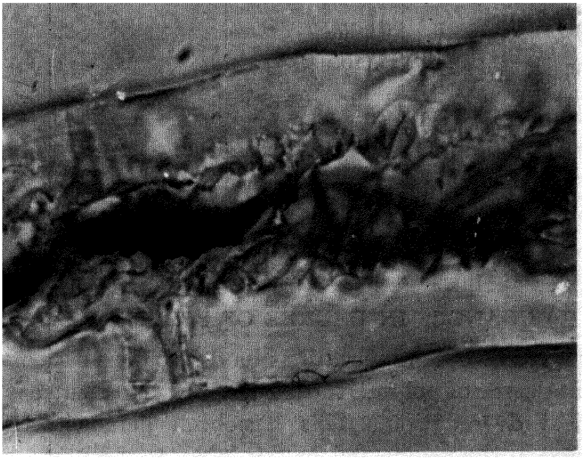

Fig. 44. Penetration of secondary wall of cotton fiber and invasion of lumen by fungi (Siu[204]).

Because of characteristic differences in growth and multiplication, bacteria attack the fiber in a different, though still localized, fashion. Bacteria are particulate rather than filamentous like fungi. Instead of growing by extension at the filament tip as do the fungi, bacteria generally simply

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[201] A. Imshenetskii and L. Solntzeva, *Bull. acad. sci., U.R.S.S., Classe sci. math. et nat., Ser. biol.*, **1936**, 1115.

[202] R. Y. Stanier, *Bact. Revs.*, **6**, 143 (1942).

[203] G. Fåhraeus, *Symbolae Botan. Upsalienses*, **9**, No. 2, 128 pp. (1947); *Chem. Abstracts*, **42**, 5504 (1948).

[204] R. G. H. Siu, *Textile Research J.*, **20**, 281 (1950).

enlarge somewhat in size. This enlargement is followed by a fission into two daughter cells. These cells adhere to the fiber and pit their way from the surface inwards. The cellulose is dissolved away at the point of contact. The process can be envisioned from the photomicrograph of a bacterially degraded fiber (Fig. 45). The imprint of the bacterial cells resulting in a saw-toothed surface of the fiber is evident.

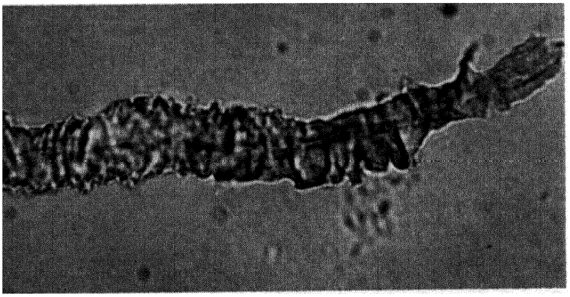

Fig. 45. Bacterially degraded cotton fiber (Siu[204]).

(b) CHANGES IN DEGREE OF POLYMERIZATION

The above microscopic observations have also been supported by studies on changes in degree of polymerization (D.P.). No change is noted during microbiological degradation. This has been demonstrated for cotton fabrics exposed in the field[205] and in the laboratory.[206–208] In this respect the action of microorganisms is unlike that of acids. In the latter case, there is a decrease of D.P. with time,[209,210] indicative of a scission of the polysaccharide chain.

Typical data on the fluidity of microbiologically degraded cotton fabrics are given in Table 15.

The data in the table are in contrast to results from measurements on the fluidity of acid-degraded cloth. In the latter case, a cloth with a 40% loss in strength would show a fluidity of about 20 rhes. A fabric degraded by sunlight would also indicate the same order of change in fluidity at 40% strength loss.

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[205] E. S. Barghoorn, *Microbiological Series, Report No. 4*, Research and Development Branch, Office of The Quartermaster General, Washington, June, 1946.

[206] N. Gralén, *Medd. Svenska Textilforskningsinst., Göteborg*, **No. 4** (1947).

[207] W. G. MacMillan and S. N. Basu, *J. Textile Inst.*, **38**, T350 (1947).

[208] J. D. Dean and R. K. Worner, *Am. Dyestuff Reptr.*, **36**, 405 (1947).

[209] G. F. Davidson, *J. Textile Inst.*, **34**, T87 (1943).

[210] M. L. Wolfrom, J. C. Sowden, and E. N. Lassettre, *J. Am. Chem. Soc.*, **61**, 1072 (1939).

TABLE 15

Strength Loss and Fluidity of Cotton Fabric Degraded by Microorganisms

Organism	Strength loss, %	Cupri-ethylenediamine fluidity in rhes
None	0	2.2
Diplodia sp.	49	2.0
Cylindrocarpon soparium	77	2.1
Cytosporina sp.	84	2.3
Colletotrichum sp.	96	2.2
Curvularia lunata	100	2.1

The microbiological results can be explained in the following manner: The cellulose molecule is rapidly digested in localized areas into water-soluble residues, which do not affect the D.P. The D.P., therefore, actually represents the value for the residual undegraded cellulose. Current thinking is not unanimous on this score, however. There are others who claim that a decrease in D.P. of cellulose actually occurs during decomposition by microorganisms.[211–213]

(c) RATE OF ATTACK ON CRYSTALLINE AND AMORPHOUS CELLULOSE

In the degradation of cellulose, microorganisms release enzymes, which are the responsible chemical agents.[214–216] There seems to be little question but that these enzymes degrade amorphous cellulose at a faster rate than the more crystalline cellulose. The rate of breakdown of cellulose samples by cellulolytic enzymes from snails, for example, varies inversely with the degree of crystallinity.[217] Likewise, the susceptibility of viscose to cellulolytic enzymes is decreased by stretching during its preparation.[218] Since stretching increases the degree of orientation, the observations seem to be in harmony with results of other work on crystallinity. Comparable results were observed with microorganisms acting on cotton mercerized with

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[211] R. E. Rogers, H. G. Wheeler, and H. Humfeld, U. S. Dept. Agr., *Tech. Bull.* **726** (1940).

[212] T. F. Heyes and H. S. Holden, *J. Textile Inst.*, **23**, T79 (1932).

[213] G. A. Greathouse, *Textile Research J.*, **20**, 227 (1950).

[214] G. Fåhraeus, *Experientia*, **2**, 413 (1946).

[215] B. Norkrans, *Symbolae Botan. Upsalienses*, **11**, 5 (1950); *Chem. Abstracts*, **45**, 6704 (1951).

[216] P. R. Saunders, R. G. H. Siu, and R. Genest, *J. Biol. Chem.*, **174**, 697 (1948).

[217] P. Karrer and P. Schubert, *Helv. Chim. Acta*, **11**, 229 (1928).

[218] O. Faust, P. Karrer, and P. Schubert, *Helv. Chim. Acta*, **11**, 231 (1928).

and without tension,[219] as well as on stretched-spun and parallel-spun cuprammonium rayon.[212]

In this connection, recent results[220] are worthy of note. When cotton fibers are soaked in cellulolytic enzyme preparations, the interfibrillar areas along spiral planes seem to be preferentially dissolved at the early stages. This is of considerable interest in view of the contention[221] that the bulk of the amorphous cellulose of the cotton fiber resides in the interfibrillar regions and that the fibrils proper are mainly crystalline.

(d) BIOCHEMICAL TRANSFORMATIONS OF THE CELLULOSE MOLECULE

Although the suggestion has been made[222] that the initial steps in the transformation of the cellulose molecule involve an oxidation of the primary hydroxyl group to a carboxyl group, analyses of existing data[202,223] support the hydrolytic process postulated in 1912.[224] Originally, it was thought[224] that only one enzymic step is involved in the solubilization of cellulose. The enzyme which is presumably responsible for the conversion of cellulose to cellobiose was named "cellulase."

Recent studies[225,226] have shown that the historical term "cellulase" may include at least two distinct types of enzymes. The first type seems to make the cellulose molecules available for reaction. The other type hydrolyzes the linear polysaccharide into sugars. The term cellulase was reserved for the *first* enzyme in the chain[204]; pending further identification, the enzyme(s) responsible for hydrolysis of the linear polysaccharide was named Cx.[225]

Explanations of the mechanism of action of cellulase on the native cellulose molecule are beset with ancillary controversies. There are two alternative hypotheses. One involves the assumption of the presence of other covalent bonds in addition to the 1,4-glucosidic linkages in the native cellulose molecule. Such linkages have been postulated by several investigators[227,228] but have been vigorously questioned by others. The enzyme

[219] O. Faust and P. Karrer, *Helv. Chim. Acta*, **12**, 414 (1929).

[220] R. Blum and W. H Stahl, *Textile Research J.*, **22**, 178 (1952).

[221] C. W. Hock, *Textile Research J.*, **20**, 141 (1950).

[222] S. Winogradsky, *Compt. rend.*, **183**, 691 (1926); *Ann. inst. Pasteur*, **43**, 549 (1929).

[223] A. G. Norman and W. H. Fuller, *Advances in Enzymol.*, **2**, 239 (1942).

[224] H. Pringsheim, *Z. physiol. Chem.*, **78**, 266 (1912).

[225] E. T. Reese, R. G. H. Siu, and H. S. Levinson, *J. Bact.*, **59**, 485 (1950).

[226] H. S. Levinson and E. T. Reese, *J. Gen. Physiol.*, **33**, 601 (1950).

[227] A. af Ekenstam, *Ber.*, **69**, 549 (1936).

[228] L. A. Hiller, Jr., and E. Pacsu, *Textile Research J.*, **16**, 243, 318, 490, 564 (1946)

cellulase would accordingly sever the nonglucosidic linkages to provide linear polysaccharide for further action by Cx. However, this leads directly into the controversy on the structure of the native cellulose molecule, from which the biochemist should stand aside and await clarification by the cellulose chemists.

On the other hand, if one assumes that native cellulose does not possess polymerizing covalent bonds other than the glucosidic type, then one can postulate the action of cellulase as breaking hydrogen bonds or swelling the cellulose. It would serve to tear the individual cellulose molecules away from the crystalline matrix in the cotton fiber. The free linear molecule would then be subjected to the attack of Cx. This hypothesis is consonant with the conventional concept of the linear polysaccharide structure of cellulose. It does require, however, the difficult postulation of a "hydrogen-bondase," which would be an unusual enzyme indeed! At the present time, there is no rigorous evidence to hypothesize additional mechanisms nor to rationalize further about these two alternate theories regarding the action of cellulase.

More is known about the action of Cx in hydrolyzing the linear polysaccharide. The action is highly specific with regard to molecular structure. Almost any chemical substitution on the cellulose molecule should prevent the activity of Cx, as long as every anhydroglucose unit reacts. This has been demonstrated for acetyl, butyl, cyanoethyl, methyl, ethyl, *p*-toluenesulfonyl (tosyl), iodo-*p*-toluenesulfonyl (iodotosyl), carboxymethyl, and other derivatives.[229] It appears that initial scission can occur anywhere along the chain. A free anhydroglucose unit in an otherwise substituted chain would be attacked. Cellobiose has been identified at an early stage in the decomposition effected by Cx and precedes glucose.[224,230,231] With certain organisms it appears that glucose may be formed directly from the linear polysaccharide without the formation of cellobiose as an intermediate.[197] The reverse has also been observed; cellobiose has been the direct hydrolysis product of Cx without further breakdown to glucose outside of the bacteria. But proof is still needed on this score. In any case, the sugars are finally absorbed by the microorganism and metabolized.

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[229] R. G. H. Siu, R. T. Darby, P. R. Burkholder, and E. S. Barghoorn, *Textile Research J.*, **19**, 484 (1949).

[230] R. E. Hungate, *J. Bact.*, **48**, 499 (1944).

[231] H. S. Levinson, G. R. Mandels, and E. T. Reese, *Arch. Biochem. Biophysics*, **31**, 351 (1951).

(e) METHODS OF PREVENTION OF DEGRADATION

The principal cellulosic materials for which methods of preservation are being developed are wood and fabrics. Some attention is also being devoted to paper and cellulosic films.

Theoretical analysis of the mechanism of decomposition suggests four possible approaches toward preservation. The first obvious possibility is preventing the organism from making intimate contact with the cellulosic substrate. Evidence suggests that a direct contact between microorganism and cellulose is necessary for decomposition. If an inert barrier can be interposed between the two, some protection should result. Resin coatings or impregnations have been tried with some success with cotton fabrics. The add-on weight is higher than desirable, and the fabrics show a "boardy hand," that is, the fabrics are stiffened and their draping property is adversely affected. As a result, this approach has not gained commercial acceptance for cotton fabrics. No systematic studies have been made on paper and wood.

The second and most practical method is the use of inhibitors toxic to the invading microorganisms. Over a thousand chemical compounds have been tested for use in cotton fabrics alone. Most of the same fungicides have been examined on wood. Out of these extensive empirical studies over centuries have emerged fairly satisfactory compounds. Creosote, copper naphthenate, copper hydroxyquinolinolate, and pentachlorophenol derivatives are examples of the more successful ones. The use of toxic inhibitors is beset with several limitations. One is their toxicity to humans. It is no mean task to find a compound toxic to one form of life, such as bacteria, and not to another form, such as man, and yet possessing the practical traits of availability, stability, cheapness, and lack of odor and color. Leachability is another decided disadvantage. To be toxic to microorganisms, the compound must be water soluble at least to an extent enabling it to penetrate the cell and poison its protoplasm. A delicate balance of properties is needed to strike a point of solubility just sufficiently high for the exercise of toxic action and yet sufficiently low for resistance to rain. Still a third obstacle over which considerable research is being carried out is the existence of strains of organisms resistant to specific compounds. In this regard, new efforts are being directed to the use of combinations rather than single compounds.

A variant of the use of toxic inhibitors is the possibility of chemicals which specifically inhibit the cellulolytic enzymes secreted by the organism. These enzyme inhibitors have the theoretical advantage over the general class of fungicides in that they should be effective against a wide spectrum of microorganisms. It is presumed that the same type of cellulolytic enzyme is secreted by all microorganisms. A compound effective against the action of one species should do the same for all species. So far, however, this approach has been confined to laboratory experimentation. It is far distant from commercialization.

The final technique is a chemical modification of the cellulosic substrate to provide resistant cellulose derivatives either on the surface or in the more accessible and amorphous regions. Theoretically, the idea has promise. The resulting treatment should be permanent, nontoxic to humans, and effective against a wide array of microorganisms. As long as a firm chemical combination exists on the accessible portions of the material to the extent of a substituent on every anhydroglucose unit, the substrate ought to be resistant. One can extrapolate from this thought to another possible advantage. Substituents can be chosen, which by their very nature impart additional desirable properties to the substrate other than mildewproofing. Thus, hydrophobic groupings may couple water repellancy with mildew resistance. The coupling of flame resistance with mildewproofing by this general technique became a commercial practice with cotton fabrics only during the last war. The method, however, has not been evaluated for wood and paper. All in all, it is still primarily a laboratory affair today, although the inherent potential advantages are there.

6. Mechanical Degradation

L. F. McBurney

Grinding, milling, and cutting are common unit processes in the chemical industry and are employed in order to achieve both size reduction and an increase in surface area of the substance being so treated. Application of these processes to the majority of solid organic and inorganic chemicals does not cause any deep-seated chemical or physical changes. Any increase in the relative reactivity of the products can be accounted for on the basis of a more rapid solubility due to particle size or a greater adsorbability caused by increased surface area. When these same processes are applied to high polymers such as cellulose, starch, natural silk, and polystyrene, however, the size reduction is also accompanied by physical and chemical alterations of the polymer. These alterations may occur in the form of crystal lattice deformation and concurrent reduction in degree of polymerization (D.P.), or they may be less severe and result only in minor changes in D.P. As an example, insignificant strength losses are encountered during the mechanical processing of cotton, whereas major degradation results from grinding operations such as ball milling.

(a) DEGRADATION ACCOMPANYING THE MECHANICAL PROCESSING OF COTTON

The physical damage to the cotton fiber during mechanical processing from seed to yarn was demonstrated first by Clegg.[232] She established, by means of the Congo red staining test, that there was a progressive increase in the number of bruised and torn fibers as the cotton was processed. Whitwell and coworkers[233,234] have attempted to evaluate, by means of viscosity measurements, the extent of chemical degradation in each step of the mechanical processing of cellulose. Their results would indicate that the majority of degradation occurs in the breaker and intermediate picker as shown in Figure 46. The magnitude of these measured changes is, however, subject to the error involved in attempting to measure reproducbly the intrinsic viscosity of materials of such high molecular weight (i.e.,

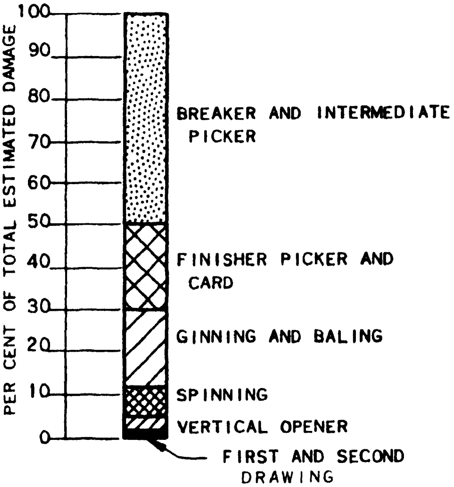

Fig. 46. Per cent of total estimated damage attributable to individual operations in the mechanical processing of cotton (Krieble and Whitwell[233]).

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[232] G. G. Clegg, *J. Textile Inst.*, **31**, T49 (1940).

[233] J. G. Krieble and J. C. Whitwell, *Textile Research J.*, **19**, 556 (1949).

[234] J. C. Whitwell, T. Lemiszka, and V. L. Hughes, *Textile Research J.*, **21**, 556 (1951)

intrinsic viscosity of 28–30), and since the total measured viscosity change was only 26%, this degradation, if real, at such a high level of D.P. would have no effect upon the physical properties of the cellulose.

Cotton may show chemical degradation during normal processing as a result of mechanical damage. This effect is not very large, however, and for most purposes can be considered negligible when compared with the degradation which can be encountered in subsequent processes such as bleaching.

(b) DEGRADATION DURING THE MILLING OF CELLULOSE

The powdering of cellulose by grinding in a vibratory ball mill (*Schwingmuhle*) has been studied extensively by several investigators,[235–240] and severe degradation has been shown to accompany this operation. Microscopic examination reveals two characteristic products of mechanical disintegration. Initially, the fibers underwent a marked fibrillation into very fine fibrils. This was followed by the production of a "cellulose powder" which did not possess any clearly recognizable structure. On continued milling, the powder form predominated to the extent that after 30 min. the largest particles remaining had a major dimension of no more than 10μ. This change in size and character is illustrated[241] in Figure 47, from which it can be seen that grinding beyond 30 min. had no appreciable effect upon particle size.

The powdery modification of cellulose has undergone extensive changes in its physical and chemical properties. The x-ray diffraction pattern, for example, has changed from that of cellulose I, at a degree of subdivision corresponding to A in Figure 47, to the broad diffuse band characteristic of amorphous cellulose corresponding to the powder illustrated in C and D of Figure 47. This crystal lattice deformation is accompanied by an increase in fluidity, as well as in moisture absorption, and a slight increase in carboxyl content as shown in Figure 48.

The fluidity–time curve is indicative of major chain scission, whereas the moisture absorption increase is the direct result of the reduction in crystallinity of the cellulose. The small change in carboxyl content is not extremely significant except as supporting evidence for the contention that the degradation is primarily mechanical rather than oxidative in character.

[235] K. Hess, H. Kiessig, and J. Gundermann, *Z. physik. Chem.*, **B49**, 64 (1941).

[236] E. Steurer, *Z. physik. Chem.*, **B47**, 127 (1940).

[237] E. Steurer and K. Hess, *Z. physik. Chem.*, **193**, 248 (1944).

[238] E. Husemann and A. Carnap, *Makromol. Chem.*, **1**, 158 (1947).

[239] P. H. Hermans and A. Weidinger, *J. Am. Chem. Soc.*, **68**, 2547 (1946).

[240] F. F. Morehead, *Textile Research J.*, **20**, 549 (1950).

These powdery celluloses will not retain their amorphous structure unless they are protected from moisture since they undergo rapid recrystallization when exposed to water vapor. The recrystallized product shows the cellulose II (or hydrate cellulose) diffraction pattern, and measurements indicate a degree of crystallinity of 30 to 40%.

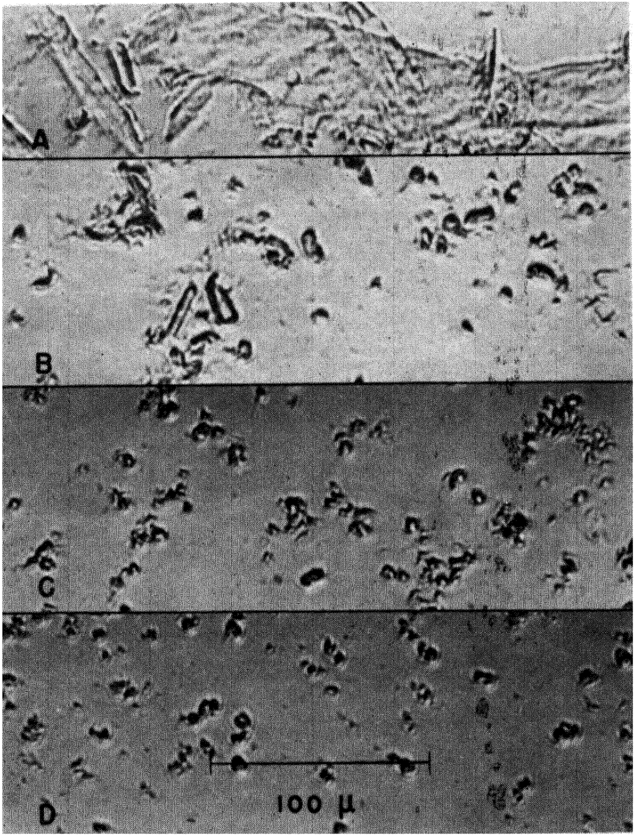

Fig. 47. Cotton ground and then mulled in mineral oil (Forziati, Stone, Rowen, and Appel[241]). A, ground in Wiley mill to pass 20-mesh screen; B, as in A, and in addition, ground in vibratory ball mill for 15 min.; C, as in B, but ground for 30 min.; D, as in B, but ground for 1 hr.

The solubility of milled cellulose is greatly increased so that the cellulose powder is completely and readily soluble in 1 *N* NaOH. This behavior would again be anticipated from the combined effects of D.P. reduction and loss of crystallinity.

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[241] F. H. Forziati, W. K. Stone, J. R. Rowen, and W. D. Appel, *J. Research Natl. Bur. Standards*, **45**, 109 (1950).

The mechanism by which the mechanical degradation occurs is not completely delineated, but it has been attributed to oxidation,[242] hydrolysis,[242] and mechanical rupture.[235,237] Oxidation has been reasonably well disproved by conducting parallel runs in nitrogen and air[237] with no chemical and physical differences being noted. This observation is further supported by infrared analysis[241] of the cellulose powder, which fails to show the presence of the carbonyl function in the molecule, and by the low carboxyl content demonstrated by chemical analysis.

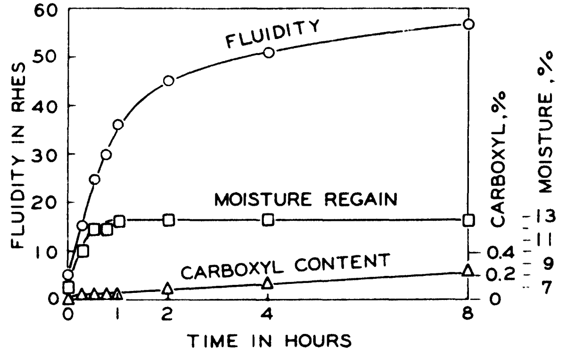

Fig. 48. Cuprammonium fluidity, moisture regain at 65% relative humidity at 21°C., and carboxyl content of cotton as functions of the time of milling in a vibratory ball mill (Forziati, Stone, Rowen, and Appel[241]).

Hydrolytic mechanisms fail to offer an adequate explanation since the rate of degradation is independent of temperature,[237] that is, it has a zero temperature coefficient. Hydrolytic reactions, on the other hand, all show rather high temperature coefficients, which fact is incompatible with the observed behavior of the mechanical degradation.

The most likely explanation appears to be that this type of degradation of cellulose is strictly a mechanical effect. The energy required to bring about the physical and chemical changes would be produced by impact or stress cycling. Hess and Steurer[237] showed that the kinetic energy available from the impact of the balls on the cellulose fiber, if converted directly to molecular vibrational energy, was sufficient to cause rupture of the primary valence bonds. By means of the Congo red test some evidence is obtained which supports a mechanical transfer of energy rather than a

[242] K. H. Meyer, *Natural and Synthetic High Polymers* (High Polymers, Vol. IV), 2d ed., Interscience, New York-London, 1950, p. 398.

thermal one. In this test the most pronounced color intensity will occur at damaged positions, showing spots or streaks at points of mechanical damage and a regular spiral pattern when the fiber has been attacked by heat. In no instance has the latter pattern been observed. It can be concluded, therefore, that rupture of the cellulose chain is the result of mechanical action and is not a thermal phenomenon.

(c) DEGRADATION OF CELLULOSE BY ULTRASONIC WAVES

The degradative effect of ultrasonic waves on cellulose and cellulose derivative solutions has been well established. Prudhomme and Grabar[243] have investigated this action with aqueous solutions of carboxymethyl cellulose and have shown that the D.P. is decreased as measured by viscosity changes. They have also observed that the effect is truly a mechanical one and not the result of oxidation by hydrogen peroxide; this was established by comparing the reaction in air and in hydrogen and showing that the degradation is independent of these two variables, and dependent solely upon time under standard conditions.

A similar investigation with viscose solutions was conducted by Sobue and Ishikawa[244] who observed that the depolymerization is dependent upon solution concentration, and decreases as the concentration is increased.

Fibrous cellulose, on the other hand, shows no degradation when exposed to ultrasonic waves.[245] In this case the action is similar to that of beating (see Chapter VIII), with viscosity showing no decrease. Microscopic investigation, however, shows an appreciable development of spirally wound fibrils. It can be concluded that under these conditions fibrous cellulose behaves as though it had been subjected to a normal beating process with the exception that no cutting action is observed.

The effect of mechanical treatments on cellulose can be summarized by saying that the milling reaction is a degradative process comparable in its magnitude to hydrolysis, oxidation, thermal degradation, or photochemical deterioration. Under the conditions of ball milling, cellulose undergoes a lattice structure deformation, chain scission, increase in solubility, and an increase in moisture absorbability. Other mechanical treatments such as occur during the normal processing of cotton are much less severe, and can be considered negligible in comparison to the better known degradative processes.

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[243] R. O. Prudhomme and P. Grabar, *J. chim. phys.*, **46**, 667 (1949).

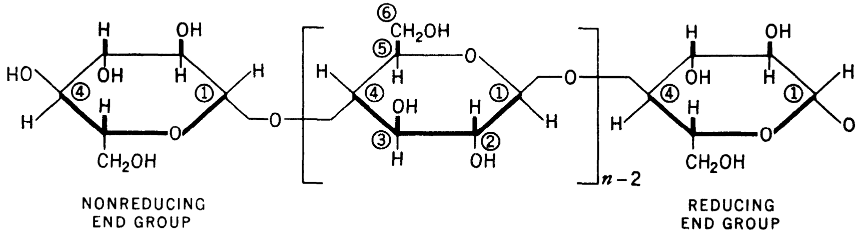
[244] H. Sobue and K. Ishikawa, *J. Chem. Soc. Japan*, Pure Chem. Sect., **71**, 103 (1950).

[245] F. W. Simpson and S. G. Mason, *Pulp & Paper Mag. Can.*, **51**, No. 8, 70 (1950).

D. END GROUPS

Arnold M. Sookne and Milton Harris

According to the present-day generally accepted concept, evidence for which has been summarized in Section B of this Chapter III, cellulose consists of long chains of the condensation products of β-glucose as shown in the following scheme:



It is apparent from this structure that both terminal glucose residues are distinguished from those in the body of the chain, one by the presence of a reducing hemiacetal group, the other by the presence of an extra secondary hydroxyl group. The presence of the former groups in native cellulose has never been conclusively demonstrated, probably because they are few in number, and may be destroyed during purification of the cellulose. The presence of the extra hydroxyl group at the nonreducing end appears to have been proved.

Cellulose, as it is generally encountered in industry, is in a more or less degraded form and for this reason, depending on the type of degradation, may or may not have end groups such as those described above. If the degradation is produced by strictly hydrolytic cleavage of the cellulose chains, then the system will remain unchanged from the standpoint of types of end groups. Thus, at each point of cleavage, one reducing and one nonreducing terminal group are formed. On the other hand, cleavage of the chains by other degradation processes, such as by oxidation (see Subsection C-3 of this Chapter III), may result in the formation of very different types of terminal groups.

From the foregoing, it is seen that the determination of the number and type of terminal groups is of interest not only from the point of view of the molecular structure and average chain length of the molecules, but also from the technological point of view. In addition, since a number of the methods for end-group determination involve measurements on undissolved cellulosic materials, the data regarding molecular chain length gained from these methods are also of interest in that they provide confirmation of results obtained by physicochemical methods which involve assumptions relative to the state of solution of the material.

The various methods which have been used in investigations of the end groups are discussed in the following text.

1. Reducing Type of End Group

A number of methods have been proposed for the estimation of the reducing type of end group. Interpretation of the results obtained with these methods in terms of molecular chain lengths involves the following assumptions: (1) each chain contains a terminal hemiacetal group; (2) all of the reducing power is contributed by these terminal groups; (3) the method used produces no new terminal groups through cleavage processes. In general, all of these assumptions are open to question, as will be brought out in the subsequent discussion.

The most widely used method has been the well-known "copper number method" of Schwalbe,[1] which depends on the reduction of copper from the cupric to the cuprous state by the cellulosic material (see Chapter XII). The original procedure has frequently been modified but, despite numerous improvements, it still leaves much to be desired. The copper number can at best be considered to be only a rough measure of the content of reducing groups of a cellulosic material. The results obtained by this method, however, have more significance when the method is applied to a homologous series of samples prepared by similar treatments.

A similar method which depends on the reduction of silver from the ionic to the metallic state by the cellulosic material was brought forth by Götze.[2] There are not sufficient data available for a complete evaluation of the method, but it is apparent that the amount of silver reduced increases indefinitely with the time of treatment, and no satisfactory method of correcting for this effect is available.

Another group of methods depends on the reaction of the reducing aldehyde groups with reagents that form condensation products with these groups. In the method of Staud and Gray,[3] the cellulosic material is allowed to react with phenylhydrazine acetate, and the nitrogen content of the product is taken as a measure of the number of reducing groups. These authors showed that an equilibrium value of the nitrogen content can be reached, and that there is fair agreement between phenylhydrazine numbers and copper numbers for a series of widely different samples. The method has the advantage that the cellulose is probably not severely degraded during the treatment. However, since the samples used by these investigators were not characterized by other measurements, it is difficult to evaluate the quantitative aspects of the method. The increase in nitrogen content of a cellulosic material after reaction with phenylhydrazine was also used by Bergmann and Machemer[4] as a measure of content of reducing end groups. They obtained good agreement between the content of reducing groups as determined by this method, and by their iodometric method which is discussed below. In addition, there have been numerous efforts to measure the content of reducing groups of hydrocellulose and oxidized celluloses by reacting the material with substituted hydrazines, sodium bisulfite, and other reagents that form condensation products with aldehyde groups. In a variation of this method, Geiger and Wissler[5] condensed the aldehyde groups of hydrocellulose with a hydrazide, and then reacted the product with a dyestuff such as picric acid. Subsequent removal and colorimetric estimation of the picric acid was found to provide a quantitative measure of the reducing end groups.

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[1] C. G. Schwalbe, *Ber.*, **40**, 1347 (1907).

[2] K. Götze, *Melliand Textilber.*, **8**, 624, 696 (1927).

The reaction of cellulose with ethyl mercaptan (ethanethiol) in the presence of fuming hydrochloric acid was used by Wolfrom[6–9] and coworkers to determine the number of free aldehyde end groups produced in the progressive degradation of cotton. Under the conditions of their experiments, the reaction

$$R_{\text{cell}}CHO + 2C_2H_5SH \longrightarrow R_{\text{cell}}CH(SC_2H_5)_2 + H_2O$$

takes place, and the extent of mercaptal formation is indicated by the sulfur content of the cellulosic product. The molecular weights of the mercaptalated products as a function of the time of reaction were determined by both sulfur and viscosity determinations, and the correspondence between these values indicates that the method is a reliable measure of end groups. Because of the continual degradation of the sample by the strong acid solution used, it is necessary to extrapolate to zero time to obtain an estimate of the degree of polymerization of the starting material. An extrapolation value of 400 was obtained for the average degree of polymerization (D.P.) of a methyl cellulose obtained by methylation of a commercial cellulose acetate, but no estimate for the molecular weight of native cellulose has been obtained by this method.

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[3] C. J. Staud and H. LeB. Gray, *Ind. Eng. Chem., Anal. Ed.*, **1**, 80 (1929).

[4] M. Bergmann and H. Machemer, *Ber.*, **63B**, 316 (1930).

[5] E. Geiger and A. Wissler, *Helv. Chim. Acta*, **28**, 1638 (1945).

[6] M. L. Wolfrom and L. W. Georges, *J. Am. Chem. Soc.*, **59**, 282 (1937).

[7] M. L. Wolfrom, L. W. Georges, and J. C. Sowden, *J. Am. Chem. Soc.*, **60**, 1026 (1938).

[8] M. L. Wolfrom and J. C. Sowden, *J. Am. Chem. Soc.*, **60**, 3009 (1938).

[9] M. L. Wolfrom, J. C. Sowden, and E. N. Lassettre, *J. Am. Chem. Soc.*, **61**, 1072 (1939).

Hiller and Pacsu[10,11] proposed the use of a solution of dilute potassium permanganate in 0.25 *N* H_2SO_4 to oxidize selectively the reducing end groups in cellulose. This procedure has been criticized by Meller,[12] whose data indicate that permanganate consumption did not reach a limiting value under the prescribed conditions, and varied with the concentration of permanganate or sulfuric acid. Husemann and Consbruch[13] have also criticized the method, and have shown that glucose and other reducing sugars remain substantially unoxidized under the conditions of Pacsu's end-group determination.

The most promising methods, from a quantitative standpoint, depend on the ability of alkaline iodine solutions to oxidize the reducing aldehyde groups to carboxyl groups. Such methods involve relatively simple volumetric procedures, in sharp contrast with the laborious procedures for estimating the nonreducing terminal groups. They suffer however, from the disadvantages common to most heterogeneous reactions.[14] The first application of this reaction to cellulosic materials was made by Bergmann and Machemer[4,15] after they had demonstrated that it gave stoichiometric results with aldohexoses, disaccharides, and a number of sugar acetates. The claims of these investigators that the iodine consumed by cellulose is selectively confined to the oxidation of free aldehyde groups to carboxyl groups, and that the reaction is of a stoichiometric nature have been disputed, especially by Hess and his coworkers,[16] Brissaud,[17] and Sakur-

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[10] L. A. Hiller and E. Pacsu, *Textile Research J.*, **16,** 318 (1946).

[11] L. A. Hiller and E. Pacsu, *Textile Research J.*, **16,** 490 (1946).

[12] A. Meller, *Tappi,* **33,** 11 (1950).

[13] E. Husemann and U. Consbruch, *Makromol. Chem.*, **5,** 179 (1950).

[14] A. R. Martin, L. Smith, R. L. Whistler, and M. Harris, *J. Research Natl. Bur. Standards,* **27,** 449 (1941); *Am. Dyestuff Reptr.*, **30,** 628 (1941).

[15] M. Bergmann and H. Machemer, *Ber.*, **63B,** 2304 (1930).

[16] K. Hess, K. Dziengel, and H. Maass, *Ber.*, **63B,** 1922 (1930).

[17] L. Brissaud, *Mém. poudres,* **25,** 222 (1932–3); **27,** 214 (1937).

ada.[18] The principal criticisms have been that the consumption of iodine does not cease at any given time but proceeds more or less indefinitely, and that, accordingly, the reaction is not stoichiometric.

The iodometric method has been reinvestigated by Martin, Smith, Whistler, and Harris,[14] who found that the above-mentioned criticisms were valid. A study of the factors which influenced the consumption of iodine by glucose and by cotton celluloses revealed that the values obtained depended on a number of conditions; for example, the length of time the reaction was allowed to proceed, the temperature, and the pH values of the iodine solutions. On the basis of these experiments, studies on the rate of oxidation of hydrocellulose at 0°C. and pH 10.6 were undertaken. It was found that there is an initial rapid reaction in the first hour followed by a secondary reaction during which iodine is consumed at a very much lower but practically constant rate. Cotton cellulose showed only a slight initial reaction with iodine, but after 1 hr. exhibited a secondary reaction of the same rate as the hydrocellulose. By applying a correction for the amount of iodine consumed in the secondary reaction, it was possible to estimate the iodine utilized in the oxidation of aldehydic groups. Iodine utilized in this way converted aldehydic to carboxylic groups; therefore, an independent check of the value obtained with iodine was readily obtained by the estimation of the carboxyl groups thus formed. Methods for estimating carboxyl groups are described in Chapter XII.

Application of this method to cotton, purified with a 1% solution of sodium hydroxide for 8 hr. according to the procedure of Corey and Gray,[19] indicated that cotton cellulose does not contain a measurable number of terminal reducing groups. However, the possibility that aldehyde groups may have been present in the cellulose before purification of the fiber cannot be overlooked, although some arguments against this possibility have been presented.[20]

Since hydrolytic degradation of cellulose results in the formation of reducing group at each point of cleavage, the method also offers a means of estimating molecular weights at various stages of degradation by use of the following equation:

$$M_n = \frac{W}{n\left(1 + \frac{\alpha M_{n_0}}{162}\right)}$$

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[18] I. Sakurada, *J. Soc. Chem. Ind., Japan*, **36**, Suppl. binding, 279 (1933).

[19] A. B. Corey and H. LeB. Gray, *Ind. Eng. Chem.*, **16**, 853 (1924).

[20] A. M. Sookne and M. Harris, *J. Research Natl. Bur. Standards*, **26**, 205 (1941); *Am. Dyestuff Reptr.*, **30**, 107 (1941).

where M_n = the number-average molecular weight
M_{n_0} = the number-average molecular weight of the original sample
W = the weight of cellulose
n = the number of moles of cellulose originally present
α = the degree of hydrolysis = the fraction of the original glucosidic linkages which have been hydrolyzed

Application of the method[14] to a series of progressively degraded hydrocelluloses, the value of n being determined viscometrically, yielded molecular weight values which were proportional to those determined from viscosity measurements, a result which indicates that the iodometric method furnishes a measure of relative molecular size for this type of cellulose.

A somewhat similar series of experiments was performed by Geiger and Wissler,[5] using the method described above. These authors studied a series of progressively degraded hydrocelluloses, and estimated the molecular weights by the content of reducing end groups. The molecular weights so determined were found to agree well with values calculated from osmotic, ultracentrifugal, and viscosity measurements.

2. Nonreducing End Groups

As pointed out earlier, one terminal group of the cellulose chain is characterized by four alcoholic hydroxyl groups. This is also true of celluloses degraded by hydrolytic means but probably not for celluloses degraded by oxidative reagents.

The presence of the extra hydroxyl group in the terminal glucose residue has been the basis for many attempts to estimate molecular chain length since, on complete methylation of cellulose, such a terminal group would yield tetramethylglucose. The essential difficulty in the method is to isolate the tetramethylglucose from the large excess of trimethylglucose originating from the remainder of the chain. Denham and Woodhouse[21] early reported a trace of crystalline material in the hydrolysis product of a methylated cellulose which resembled tetramethylglucose, but later work on methylated celluloses did not confirm their observations. Irvine and Hirst[22] and Freudenberg and Braun[23] were also unable to find any trace of tetramethylglucose. This led the former investigators to postulate a ring structure for cellulose and the latter to conclude that the molecular chains of cellulose are very long. Haworth and Machemer[24] were the first definitely to isolate tetramethylglucose as the methyl glucoside derivative through a process which involved acetylation of the cellulose, conversion of the acetate to a completely methylated product, hydrolysis of the methylated cellulose, and finally conversion of the methylated glucose components into the methyl glucosides which were separated by fractional distillation. It was claimed that this procedure produced little or no scission of the chain molecules, and, on the basis of the results, it was concluded that cellulose was composed of chains of an average length of 100 to 200 glucose residues, the average of these values being regarded as the average lower limit of the size of the molecules.

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[21] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **105**, 2357 (1914).

[22] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **123**, 518 (1923).

[23] K. Freudenberg and E. Braun, *Ann.*, **460**, 288 (1928).

[24] W. N. Haworth and H. Machemer, *J. Chem. Soc.*, **1932**, 2270.

The interpretation of the results of this type of experiment in terms of the molecular weight of the starting material involves the following assumptions:

(1) Each chain contains a terminal glucose residue capable of yielding tetramethylglucose. This is probably true for undegraded celluloses and hydrocelluloses, but for certain oxidized celluloses the modification of the terminal glucose residue may be such as to render it incapable of the formation of tetramethylglucose.

(2) The tetramethylglucose is contributed solely by the terminal glucose residues described in (1). This assumption is justifiable.

(3) The procedure used produces no new terminal groups through cleavage of the molecular chains. This is probably never completely true, although it would appear that degradation may be kept low by proper control of conditions. Since for undegraded cellulosic materials the proportion of terminal groups appears to be of the order of magnitude of one part in several thousand, it is apparent that even a relatively minor amount of degradation may lead to seriously erroneous results. The possibility of degradation must therefore be considered very carefully.

The method of Haworth and Machemer[24] has been criticized by Hess and Neumann[25] on the grounds that the starting material (acetone-soluble cellulose acetate) is unsuitable for a determination of the end groups in cellulose, since a certain amount of degradation must occur in the acetylation and saponification processes. Furthermore, Hess and Neumann were unable to remove the cleavage products so obtained or to separate quantitatively the tetramethylglucose from the trimethylglucose by Haworth and Machemer's method of fractional distillation of the respective glucosides. It is difficult to evaluate these criticisms, especially since repetition of the method of Haworth and Machemer by other members of Haworth's school led to complete substantiation of the original results.[26] It seems reasonable, however, to agree with Hess and Neumann's criticism concerning degradation during acetylation and saponification, especially in view of the very low average degree of polymerization (D.P.) for cellulose obtained by the use of this method in comparison with values obtained by other methods.

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[25] K. Hess and F. Neumann, *Ber.*, **70B**, 710 (1937).

On the basis of their criticisms of the method of Haworth and Machemer, Neumann and Hess[27] developed a method which differs from the method of Haworth and Machemer in that the methylation is performed directly on the cellulose, and, in the separation of the glucosides, recourse is had to the fact that the barium salts of the phosphoric esters of the methyl trimethylglucoside and less highly methylated sugars are insoluble in petroleum ether, while that of the methyl tetramethylglucoside is completely soluble. The Neumann and Hess methylation procedure yields a product of 42% methoxyl content, corresponding to complete methylation of only about 72% of the glucose units; this must therefore be taken into account in calculations of the number of end groups in the original material.

The procedure has been applied by Hess and Neumann to various relatively undegraded samples of cotton. It was found that when air was carefully excluded during the alkaline purification pretreatment as well as during the subsequent methylation, no tetramethylglucose was obtained. It was therefore concluded that natural cotton cellulose contains no end groups, and consists of chains of infinite length or, more probably, of ring structures. A similar result was later obtained on ramie.[28] The presence of air during the alkaline pretreatment or during the methylation was found to produce numerous end groups.

The results of Hess and Neumann were substantiated by Leckzyck,[29] who reported, in addition, that thorough extraction (in the absence of air) with 9% NaOH is necessary to remove completely the fat–wax concomitants of the natural fiber, which may otherwise appear in the end-group fraction. Further, Leckzyck prepared an artificial mixture of methyl tetramethyl- and methyl trimethyl-glucosides in the proportion of 1:9300 and found that the loss of the former was only 7.7%. It was accordingly claimed that the method is at least sensitive enough to determine end groups if they appear in the proportion of only 1 part in 10,000. It is well to note, however, that Hess's data show an appreciable loss of the methyl tetramethylglucoside during the distillation processes when artificial mixtures are used.[27,30] When the number of steps in the purification process is considered, as well as the variety and quantity of complex cleavage products which may be present, the likelihood of such losses appears to be great. It is perhaps indicative of the inherent difficulties of the isolation methods that Averill and Peat[26] have substantiated Haworth and Machemer, but have been unable to repeat the results of Hess and Neumann. The most recent claims of Hess's school[31] place the minimum D.P. of cellulose at 10,000. The weight-average D.P. of cotton cellulose as obtained by Kraemer from viscosity and ultracentrifugal measurements is approximately 3500; the ultracentrifugal measurements of Gralén and Svedberg[32] place this figure at approximately 9000.

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[26] F. J. Averill and S. Peat, *J. Chem. Soc.*, **1938**, 1244.

[27] F. Neumann and K. Hess, *Ber.*, **70B**, 721 (1937).

[28] K. Hess and K. P. Jung, *Ber.*, **73B**, 980 (1940).

[29] E. Leckzyck, *Ber.*, **71B**, 829 (1938).

In subsequent studies, Haworth's coworkers[33] improved their method of fractional distillation for the separation of the methyl glucosides. They also met the criticisms of Hess by directly methylating the cellulose, and by working in an atmosphere of nitrogen.[34] Their new data show that when relatively undegraded cotton is methylated in an atmosphere of nitrogen, no tetramethylglucose is found in the hydrolysis products.[34] Somewhat paradoxically, however, they reported an end-group content corresponding to an average D.P. of 700 for a sample of cotton sliver which had been directly methylated in an atmosphere of nitrogen for fifteen successive times.[35] It must be noted, however, that the series of methylation treatments produced a large decrease in the viscometrically determined chain length. Their present (minimum) value for the average D.P. of natural cellulose (700), though considerably higher than their earlier estimates, still leaves a very large discrepancy between their results and those of Hess's school.

Experiments by Haworth and coworkers on hydrocellulose[36] and oxidized cellulose[37] indicate that the viscometrically estimated decrease of chain length that occurs during the preparation of these samples is accompanied by a corresponding and roughly proportional increase in the number of nonreducing end groups. Similarly, Hess, though unable to find end

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[30] K. Hess, D Grigorescu, E. Steurer, and H. Frahm, *Ber.*, **73B**, 505 (1940).

[31] K. Hess, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 333 (1938).

[32] N. Gralén and T. Svedberg, *Nature*, **152**, 625 (1943).

[33] E. L. Hirst and G. T. Young, *J. Chem. Soc.*, **1938**, 1247.

[34] W. N. Haworth, L. N. Owen, S. Peat, and F. J. Averill, *J. Chem. Soc.*, **1939**, 1885.

[35] W. N. Haworth, R. E. Montanna, and S. Peat, *J. Chem. Soc.*, **1939**, 1899.

[36] H. C. Carrington, W. N. Haworth, E. L. Hirst, and M. Stacey, *J. Chem. Soc.*, **1939**, 1901.

[37] G. L. Godman, W. N. Haworth, and S. Peat, *J. Chem. Soc.*, **1939**, 1908.

groups in undegraded cellulose, has suggested that the number of end groups found in technical celluloses, or in hydrocellulose and oxidized celluloses, is a reliable measure of their degradation.[30] In a more recent work,[38] however, he has stated that although a decrease in viscometrically determined D.P. is accompanied by a general increase in end groups, there is no simple frunctional relationship between the two quantities. Thus, samples of equal viscosity produced by different degradative processes (hydrolysis, oxidation, ultraviolet irradiation) may have widely different end-group contents. On the basis of these and other results, Hess has formulated a modification of the chain hypothesis which involves interchain oxygen bridges.

The lack of proportionality between end-group values and D.P.s as determined by viscosity measurements may be attributed to at least two factors. First, it must be recalled that the type of end groups produced by cleavage depends on the cleavage mechanism. Thus, in hydrolytic breakdown the production of groups capable of yielding tetramethylglucose seems unambiguous. For certain types of oxidative cleavage, on the other hand, this is very likely not the case. Thus an oxidized cellulose and a hydrocellulose of equal viscometrically estimated molecular weights could easily have different end-group contents.

Secondly, it must be considered that the end groups and viscosity methods measure different quantities, namely, number-average and weight-average molecular weights. The ratio of these two quantities is a function of chain-length distribution for any sample, and there is reason to believe that the distribution of chain lengths need not be the same for samples subjected to different degradative processes. Thus, with a fibrous material, different portions of the fiber may vary in their rates of degradation, depending on the reagent or method of degradation. The end groups and viscosity methods therefore need not give proportional results for samples degraded by different methods.

The methods described above for the estimation of nonreducing end groups suffer from two obvious disadvantages: the procedures require a long series of rather severe treatments which may easily degrade the original material, and they require the isolation of a material which is present in only minute proportions. The difficulties are clearly shown by the large and consistent differences that exist between the schools of Hess and Haworth. For relatively degraded materials, however, the difficulties are much less severe, and the data indicate that this type of end-group method should be capable of giving a reliable relative estimate of the chain length, at least for celluloses of the same general type.

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[38] K. Hess and E. Steurer, *Ber.*, **73B**, 669 (1940).

The foregoing discussion has dealt only with reducing end groups of the hemiacetal type, and nonreducing end groups capable of forming tetramethylglucose. It has been pointed out, however, that for oxidized celluloses, the latter type of group may be altered so as to render it incapable of forming tetramethylglucose. It appears that, in addition to these types of end groups, cellulose chains may under special circumstances contain acidic end groups, which are presumably carboxyl groups formed by oxidation of the hemiacetal end. Workers at the Southern Regional Research Laboratory actually isolated gluconic acid from cellulose end groups.[39] Thus, cotton purified by the American Chemical Society procedure (see Chapter XII) has been found to contain no free aldehydic reducing groups,[14] but does appear to contain a number of acidic groups corresponding to an equivalent weight of about 100,000. The acidic groups of cellulose are considered in Section E of this Chapter III.

[39] M. G. Blair and R. E. Reeves, *J. Am. Chem. Soc.*, **74**, 2622 (1952).

E. BASE-EXCHANGE PROPERTIES

ARNOLD M. SOOKNE AND MILTON HARRIS

That neutral salt solutions become acidic when passed through filter paper has been known for some time. Studies of this and related phenomena have shown that they result from the ability of cellulosic materials to engage in cation-exchange reactions which are similar to those that occur in the zeolites; thus, for example, properly activated jute has been shown to be capable of softening water.[1] It has now been clearly established that these exchange reactions are limited to cations,[1-3] and that cellulosic products exchange many cations one for another with a rapidity that is characteristic of inorganic reactions. Further, the reactions are easily reversed,[1,4,5] although cations vary considerably in their "affinity" for the fiber.[4-7]

In naturally occurring cellulosic fibers, the exchange capacity is principally accounted for by the materials, such as pectic substances and lignin,[1,8] associated with the cellulose; in fibers freed from these substances, the exchange capacity has been accounted for by acidic groups in the cellulose itself.[8,9] Some evidence has been presented which indicates that these acidic groups are carboxyl groups and that a small but definite number of such groups may be present in the original cellulose. In certain oxidized celluloses, however, the proportion of such groups becomes relatively large. An excellent general discussion of cation exchange in oxidized celluloses is given by Davidson and Nevell.[10]

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[1] D. A. McLean and L. A. Wooten, *Ind. Eng. Chem.*, **31**, 1138 (1939).

[2] P. Pascal and J. Hansot, *Compt. rend.*, **195**, 349 (1932).

[3] J. Gavoret, *Compt. rend.*, **204**, 1643 (1937).

[4] A. C. Walker and M. H. Quell, *J. Textile Inst.*, **24**, T123 (1933).

[5] A. C. Walker and M. H. Quell, *J. Textile Inst.*, **24**, T131 (1933).

[6] H. Rath and H. Dolmetsch, *Klepzig's Textil-Z.*, **41**, 475 (1938).

[7] G. F. Davidson, *J. Textile Inst.*, **39**, T87 (1948).

[8] A. M. Sookne and M. Harris, *J. Research Natl. Bur. Standards*, **25**, 47 (1940); *Am. Dyestuff Reptr.*, **29**, 333 (1940).

[9] S. M. Neale and W. A. Stringfellow, *Trans. Faraday Soc.*, **33**, 881 (1937).

[10] G. F. Davidson and T. P. Nevell, *J. Textile Inst.*, **39**, T59 (1948).

1. Exchange Reactions Involving Replacement of Metallic Cations by Each Other

A thorough investigation of the base-exchange properties of cotton has been made by Walker and Quell[4,5] in which they quantitatively determined the constituents of the ash of cotton before and after washing the fiber with water, acids, and especially dilute salt solutions. On the basis of these studies, it was concluded that in naturally occurring cellulosic materials, the acidic groups exist in the salt form,[11] the cations being, for the most part, polyvalent cations of high affinity. When the fiber in this form is immersed in a salt solution, exchange between the cations on the fiber and those in the solution occurs, the extent of the exchange depending on the relative affinities of the cations for the acidic groups, and on their concentrations. Thus, tightly bound Ca^{++} ions may be replaced by less tightly bound Na^{+} ions, if the latter appear in sufficiently high concentrations. On the other hand, the polyvalent ions Ca^{++} and Mg^{++} were found to be readily interchangeable, simply by washing the fiber with the respective Mg^{++} or Ca^{++} salts. Such exchanges are not accompanied by appreciable changes in the pH value of the solution surrounding the fiber.

Rath and Dolmetsch[6] confirmed the fact that alkali metal cations may be rather easily washed from the fiber, but that polyvalent cations like Ca^{++} adhere tenaciously unless the fiber is washed with acid or a salt solution. These investigators also studied the absorption of Ag^{+} ions by cotton from solutions of silver acetate. The amount of silver absorbed was taken as a measure of the number of carboxyl groups in the material. When applied to native cellulose, the process involves the exchange of Ag^{+} ions in the solution for the metal cations already on the fiber in accordance with the following equation:

$$R_{cell}COOM + AgA \rightleftharpoons R_{cell}COOAg + MA \qquad (1)$$

where R_{cell} COO— represents the acidic group on the fiber; M, the cations; and AgA, the silver salt used.

If the cellulose exists in the acidic form, then the reaction is:

$$R_{cell}COOH + AgA \rightleftharpoons R_{cell}COOAg + HA \qquad (2)$$

As has been pointed out by Sookne and Harris,[12] however, not all of the carboxyl groups bind silver when the cellulosic material is immersed in a dilute solution of silver acetate. Complete reaction of the carboxyl groups with the Ag^{+} ion is opposed by the competition of metallic cations in reaction 1 and hydrogen ions in reaction 2. These investigators have shown, however, that the silver titration method leads to a satisfactory estimate of the number of carboxyl groups if the titration is performed on electrodialyzed cotton (to eliminate competition from metallic cations) using a solution of the silver salt of a very weak acid (to minimize competition from hydrogen ions). Silver *o*-nitrophenolate was found to be a suitable salt.[12]

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[11] Evidence for this has also been presented by Kolthoff,[16] McLean and Wooten,[1] and Sookne and Harris.[8]

A critical comparison of the suitability of all three (*o*-, *m*-, and *p*-) silver nitrophenolates for use in the silver titration method has been made by Davidson and Nevell.[13] These authors recommend the use of silver *m*-nitrophenolate because of its higher solubility, and because it is the salt of a weaker acid, thus minimizing competition of hydrogen ions for carboxyl groups.

Farrar, Neale, and Williamson[13a] have proposed a gravimetric method for estimating carboxyl groups, based on the exchange of cations on the cellulose for uranium ions; it involves immersion of the sample in a 0.01 *M* solution of uranyl acetate. The sample of cellulose is subsequently washed, dried, and ashed, the increase in weight being taken as a measure of carboxyl content. The method has been criticized by Ant-Wuorinen,[13b] who found that the uranium salt of cellulose is hydrolyzed by thorough washing with water, so that no definite endpoint could be found.

2. Exchange Reactions Involving Replacement of Metallic Cations by Hydrogen

When the fiber in the salt form is immersed in an acidic solution, exchange of the cations already present by hydrogen ions occurs in an amount that has been shown to be dependent on the mass action law,[8] and the extent of the exchange is directly indicated by the decrease of the hydrogen-ion concentration of the solution. This procedure forms a basis for estimating the number of cations on the fiber, and hence the number of acidic groups. The process is essentially a back-titration of the acidic groups, and offers a method of preparing cellulose in the acidic form. Cellulose in this form can also be prepared by electrodialysis.[14] It has been shown, especially by Kolthoff,[15] McLean and Wooten,[1] and Sookne and Harris,[8] that the acid-binding capacity of cellulose is quantitatively determined by its content of bound cationic ash. Neale and Stringfellow[9] early made use of this principle as a means for estimating the acidic groups in various celluloses. Their procedure consisted in immersing a sample of the electrodialyzed fiber in a solution of NaOH and NaCl, and then back-titrating with HCl. The method was applied to various oxidized celluloses, and the number of carboxyl groups found was proportional to the amount of oxygen consumed in the preparation of a specific sample of oxidized cellulose. The estimated strengths of the carboxyl groups were of the proper order of magnitude for a hydroxycarboxylic acid. However, a carboxyl content of only 0.002 milliequivalent per gram was found for unoxidized standard cotton cloth. This value is much lower than that obtained by other investigators on similar materials. It should be noted that this method is essentially equivalent to titrating the salt form of cellulose with acid, in the presence of a neutral salt, thus:

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[12] A. M. Sookne and M. Harris, *J. Research Natl. Bur. Standards*, **26**, 205 (1941); *Am. Dyestuff Reptr.*, **30**, 107 (1941).

[13] G. F. Davidson and T. P. Nevell, *J. Textile Inst.*, **39**, T93 (1948).

[13a] J. Farrar, S. M. Neale, and G. R. Williamson, *Nature*, **168**, 566 (1951).

[13b] O. Ant-Wuorinen, *Paperi ja Puu* (Papper och Trä; Paper and Timber), **35B**, No. 4 (1953).

[14] A. M. Sookne, C. H. Fugitt, and J. Steinhardt, *J. Research Natl. Bur. Standards*, **25**, 61 (1940); *Am. Dyestuff Reptr.*, **29**, 333 (1940).

$$R_{cell}COOH + NaOH \rightleftharpoons R_{cell}COONa + H_2O$$

$$R_{cell}COONa + HCl \rightleftharpoons R_{cell}COOH + NaCl$$

A modification of Neale and Stringfellow's method has recently been suggested by Ant-Wuorinen.[15a] It involves washing of the cellulose with a concentrated aqueous solution of carbon dioxide, reaction of the product with a solution of NaCl under a nitrogen atmosphere, and back-titration under nitrogen of the hydrogen ions liberated, using a 0.001 *N* solution of NaOH.

The method involving titration of the salt form of cellulose with acid has been used by McLean and Wooten[1] and Sookne and Harris.[8] The former showed that the acid-binding capacity of a cellulosic material at an arbitrary pH value is proportional to the ash content, and that the exchange capacity is associated principally with the noncellulosic concomitants of the material (pectic substances, lignin, etc.). In addition, it was shown that cellulosic materials engage in no anion exchange of appreciable magnitude. The latter investigators, in their study of the cation-exchange properties of cotton, further demonstrated that the cationic ash determines the acid-binding capacity of cotton at any pH, and also that most of the ash is associated with the pectic substance in the raw fiber. The absorption of acid in solutions of any pH value was also shown to be consistent with the mass action law and the Donnan equilibrium; that is, cellulose absorbs less acid from a solution containing acid plus salt than from a solution at the same pH but containing only acid.

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[15] I. M. Kolthoff, *Pharm. Weekblad,* **58,** 233 (1921).

[15a] O. Ant-Wuorinen, *Paperi ja Puu* (Papper och Trä; Paper and Timber), **33B,** Nos. 4a and 5, 105 (1951); *Chem. Abstracts,* **47,** 6131 (1953).

A variation of the above method for estimating acidic groups involves engaging these groups with tightly bound cations, such as calcium, followed by electrodialytic determination of the cation content of the sample.[14] The interpretation of such measurements depends on whether all the valences of a polyvalent cation are engaged by the fiber. While there are some indications to the contrary,[12] the evidence shows that cellulose combines with an equal number of cations regardless of valency, rather than binding the same number of equivalents. This conclusion was reached by Rath and Dolmetsch[6] on the basis of work with sodium and calcium ions, and by Church,[16] who reacted acid-washed cellulose with a variety of mono-, di-, and tri-valent cations and then determined their ash contents. Combination with an equal number of cations corresponds for polyvalent cations to the formation of a basic salt or of a mixed salt such as $R_{cell}CaCl$.

Schmidt and coworkers[17] used a conductometric method to measure the number of carboxyl groups of various celluloses. Their method consisted of adding a quantity of dilute alkali to electrodialyzed cotton, and then titrating with acid. The number of acid groups in a sample was estimated by extrapolating the curve relating conductivity of the system to the amount of acid added. With this method, Schmidt obtained a content of carboxyl groups of 0.28% for native cellulose, the quantity being so constant for variously purified celluloses of widely different types that he proposed this property as a criterion for native cellulose. Neale and Stringfellow[9] were unable to repeat this conductometric titration, their data showing that a smooth conductivity curve, incapable of being extrapolated, is obtained. In addition, Neale and Stringfellow were unable to repeat Schmidt's direct titration of electrodialyzed cotton with NaOH. Unfortunately, Schmidt's papers do not contain any of the experimental curves but only the results of the extrapolations.

3. Exchange Reactions Involving Replacement of Hydrogen Ions by Metallic Cations

As pointed out earlier, cellulose may be obtained in the acidic form by replacement of its cations by hydrogen ions, either by treatment of the fiber with acid or by an electrodialytic process. The acidic groups of cellulose in this form can be titrated directly, a procedure which has been used for the estimation of the acidic groups in cellulose.

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[16] H. F. Church, *J. Soc. Chem. Ind.* (*London*), **66**, 221 (1947).

[17] E. Schmidt and coworkers, *Cellulosechemie*, **13**, 129 (1932); *Naturwissenschaften* **21**, 206 (1933); *Ber.*, **67B**, 2037 (1934); **68B**, 542 (1935); **69B**, 366 (1936).

Lüdtke[18] attempted to measure the content of acidic groups of rayons and pulps by titrating the cation-free fiber with dilute alkali in the presence of a large excess of calcium acetate. However, Neale and Stringfellow[9] have indicated that the method is unreliable since there is a large uncertainty in this end point, presumably because of the buffering effect of the acetate. This difficulty was also noted by Heymann and Rabinov,[19] but a modification of Lüdtke's calcium acetate method was successfully used by Yackel and Kenyon[20] to measure the carboxyl content of a series of oxidized celluloses. A critical appraisal of the calcium acetate method in comparison with other ion-exchange techniques for estimating the carboxyl content of cellulose has been provided by Davidson and Nevell.[21]

The difference in "affinity" of various metal cations for the carboxyl groups of cellulose has been noted by Heymann and Rabinov,[22] and this phenomenon has been examined in detail by Davidson.[7] The order of increasing affinity found by this author was:

$$N(CH_3)_4^+ < Li^+ < Na^+ < K^+ < Tl^+ < Ag^+ < Ca^{++}, Ba^{++}$$

At low concentrations, the affinity of the methylene blue cation was found to be much greater than that of any of the metallic cations studied.

4. Exchange Reactions Involving Dye Cations

The cations of basic dyes can engage in exchange reactions with the carboxyl groups of cellulose, and in fact this phenomenon has been made the basis of methods for estimation of such groups. The "reversible methylene blue method" of Weber and Husemann[23] measured the dyestuff absorption by passing a dilute solution of methylene blue over the acid-washed cellulose, after which the dye was released by washing with acid and was estimated colorimetrically. Davidson[24] has critically examined Weber and

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[18] M. Lüdtke, *Papier-Fabr.*, **32**, Tech.-wiss. Tl., 509, 528 (1934); *Angew. Chem.*, **48**, 650 (1935); *Biochem. Z.*, **285**, 78 (1936).

[19] E. Heymann and G. Rabinov, *Trans. Faraday Soc.*, **38**, 209 (1942).

[20] E. C. Yackel and W. O. Kenyon, *J. Am. Chem. Soc.*, **64**, 121 (1942).

[21] G. F. Davidson and T. P. Nevell, *J. Textile Inst.*, **39**, T102 (1948).

[22] E. Heymann and G. Rabinov, *J. Phys. Chem.*, **45**, 1152 (1941).

[23] O. H. Weber, *J. prakt. Chem.*, **158**, 33 (1941); E. Husemann and O. H. Weber, *J. prakt. Chem.*, **161**, 1 (1942); *Naturwissenschaften*, **30**, 280 (1942); *J. prakt. Chem.*, **159**, 334 (1942).

[24] G. F. Davidson, *J. Textile Inst.*, **39**, T65 (1948).

Husemann's results and shown the need for controlling the pH of the dye solution as well as allowing ample time for attainment of equilibrium. In its modified form, the methylene blue method[24] is regarded by Davidson as the most generally useful in studying celluloses of low carboxyl content.

The affinities for cellulose of various cations of basic dyes were also studied by Davidson,[25] using cation exchange methods. Basic dyes were found to differ widely in affinity, but all those studied were held much more tightly than the sodium ion. Exchange reactions involving dyestuffs did not conform to the law of mass action, but rather to the equation:

$$R = Kr^p$$

where R and r are ratios of the concentrations of the competing cations in the cellulose and solution phases, respectively, K is a constant, and p is a constant less than unity.

5. Modified Celluloses of High Exchange Capacity

The cation-exchange properties of phosphorylated cotton have been studied by Jurgens, Reid, and Guthrie.[26] These authors prepared a phosphorylated cellulose with a cation-exchange capacity of approximately 1 milliequivalent per gram, which approximates that of commercial zeolites and cation-exchange resins. The cation- (and anion-) exchange capacities of samples of a variety of modified celluloses were also studied by Hoffpauir and Guthrie,[27] who also measured the pH at half capacity as an indication of the useful pH range for each product.

6. Industrial Significance of Base-Exchange Capacity

The base-exchange capacity of commercial fibers, chemical celluloses, and cellulose derivatives is important in many industrial applications. The stability and electrical properties of papers for electrical condensers are profoundly influenced by the amount and nature of the bound metal ions.[28] Paper fibers acquire a negative charge in most ionic environments, due to dissociation of the bound metals.[29] This property is responsible for adhesion of positively charged rosin-size particles in the conventional beater-sizing process used in paper manufacture.[30] Concentrated solutions of cellulose derivatives containing bound metals, especially calcium, have abnormally high viscosity (Chapter X-A). The bound ash content of wood cellulose has deleterious effects on cellulose acetylability and on the stability of the resulting product.[31] These and other effects, as well as the innate scientific interest of the subject, explain the great amount of work on the base-exchange properties of cellulose during recent years.

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[25] G. F. Davidson, *J. Textile Inst.*, **41**, T361 (1950).

[26] J. F. Jurgens, J. D. Reid, and J. D. Guthrie, *Textile Research J.*, **18**, 42 (1948).

[27] C. L. Hoffpauir and J. D. Guthrie, *Textile Research J.*, **20**, 617 (1950).

[28] D. A. McLean, *Paper Trade J.*, **118**, 31 (Jan. 27, 1944).

[29] S. G. Mason, *Tappi*, **33**, 413 (1950).

[30] W. S. Wilson, *Paper Trade J.*, **119**, 47 (July 6, 1944).

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[31] C. J. Malm, *Svensk Papperstidn.*, **50**, 135 (1947).

Chapter IV

STRUCTURES AND PROPERTIES OF CELLULOSE FIBERS

A. INTERACTION AND ARRANGEMENT OF CELLULOSE CHAINS

H. MARK

All of the properties of cellulose and its derivatives, both chemical and physical, are in the last analysis determined by their chemical structure. However, the connection between some of these properties and the chemical structure is not very obvious. This is particularly true of the physical properties, such as fiber structure discussed in this Chapter IV, solubility (Chapter X-A), and mechanical properties (Chapter XI). Even the chemical properties are so dependent on physical factors that it is sometimes difficult to see the connection between the behavior of cellulose in its reactions and the chemical formula discussed in Chapter III.

It is necessary to consider in detail the nature of the intermolecular attraction between cellulose chains in order to obtain satisfactory explanations of the many phenomena that are observed. In view of the fundamental nature of this approach, it was felt that a short introduction of general character should precede the remainder of Chapter IV on "Structure and Properties of Cellulose Fibers."

Many of the complications encountered in cellulose chemistry are due to the fact that the intermolecular forces between the cellulose chains can produce a supermolecular texture or type of arrangement which profoundly influences most properties of the material. Once created, a particular arrangement is rather difficult to alter. Chemically similar samples of cellulose may therefore exhibit very different properties.

The first stage in the recognition of the possible nature of the texture or supermolecular structure of cellulose came with the discovery (around 1920) that cellulose gives well-defined x-ray diffraction diagrams.[1] As will be shown in Section B of this Chapter IV, the x-ray results demonstrated an approach to an ordered arrangement of the molecules in three dimensions that might be termed crystalline. Further progress came with the realization of the connection between mechanical properties and the ordered arrangement revealed by x-rays. This connection was further emphasized by the striking influence of stretching and relaxation on the x-ray diagram of rubber.[2] Since these discoveries were made, there has been continuous progress in the development of a theory of the behavior of polymer systems, based on the nature of the arrangement of molecules in more or less well-ordered regions. This theory is still incomplete in many of its details, but it appears to be the basically correct approach for an understanding of physical and mechanical properties.

When the early x-ray patterns were first studied, it was only natural that attention was focused on the sharper interference spots. These indicated the existence of domains where the chain molecules were ordered in three dimensions, in a degree of perfection approaching that of the crystalline state. It was not until somewhat later that it was realized that only a portion of natural cellulose fibers could be considered as belonging to these crystalline regions. The concept then arose that the "crystalline" regions were embedded in an "amorphous" matrix.[3] It became more and more apparent that the highly ordered domains could be considered as establishing cross-links between the less ordered regions, capable of preventing slippage on the application of a load. The regions of low order, on the other hand, appeared to be responsible for such phenomena as swelling in solvents and the continued deformation or creep encountered under the influence of a sustained stress. Much progress has been made in the clarification of the above picture. To a large extent, this clarification has depended on a more complete knowledge of the behavior of substances of low molecular weight. This will be discussed under the following topics.

[1] Compare P. Scherrer, *Nachr. kgl. Ges. Wiss. Göttingen*, **1918**, 96; *Chem. Abstracts*, **13**, 2624 (1919); R. O. Herzog and W. Jancke, *Ber.*, **53B**, 2162 (1920); M. Polanyi, *Naturwissenschaften*, **9**, 288 (1921); J. R. Katz, *Cellulosechemie*, **6**, 37 (1925); H. Mark, *Ber.*, **59B**, 2982 (1926).

[2] J. R. Katz, *Naturwissenschaften*, **13**, 411 (1925); E. A. Hauser and H. Mark, *Kolloidchem.-Beihefte*, **22**, 63 (1926); compare also C. W. Bunn in *Advances in Colloid Science*, Vol. 2, Interscience, New York-London, 1946, pp. 95–143.

[3] Compare K. H. Meyer and H. Mark, *Ber.*, **61B**, 1936 (1928); *Der Aufbau der hochpolymeren Substanzen*, Akadem. Verlagsgesellschaft, Leipzig, 1930; K. Hermann, O. Gerngross, and W. Abitz, *Z. physik. Chem.*, **B10**, 371 (1930); W. T. Astbury, *Trans. Faraday Soc.*, **29**, 193, 204 (1933); P. H. Hermans, *Physics and Chemistry of Cellulose Fibres*, Elsevier, New York, 1949, pp. 251–262.

1. Phase Transitions in Ordinary Organic Condensed Systems

Pure organic substances, as has long been known, form well-developed crystals with sharp reversible melting points and characteristic x-ray diagrams. Closer, more recent study of the transition phenomena in ordinary organic compounds can be briefly summarized as follows. The conditions are generally dominated by the existence of a sharp melting point above which the material behaves essentially as a Newtonian liquid of low viscosity (usually below one poise), and below which one observes exclusively the presence of more or less well-developed crystals. This melting point is characterized by a finite heat and entropy of melting and is sometimes referred to as a *transition point of the first order.* It appears that at this point the various rotatory and migratory motions of the individual molecules are liberated, whereas they are hindered below this temperature. However, x-ray studies of numerous ordinary organic compounds in the neighborhood of their melting points have demonstrated that the diffraction spots lose intensity and sharpness several degrees below the macroscopic transition point.

The current interpretation of this behavior is that an organic crystal can still outwardly appear as a solid, regularly shaped system whereas the individual molecules are already vibrating and rotating so violently that x-ray scattering does not register any sustained order in molecular domains. Upon cooling the material through the melting point, certain translational and rotational motions show a greater tendency to freeze in and form a lattice than do others. There then exists the impression of a solid body although there are still rotations of whole molecules or parts of them occurring. In certain cases, particularly if rotations with low moments of inertia exist, it has been found that the rotations degenerate into oscillations only at temperatures far below the melting point. This change gives rise to relatively sharp and well-defined *second-order or higher order transition points*, which have been frequently observed with many organic and inorganic substances.[4] It also occurs often that with decreasing temperature a different arrangement of the centers of gravity of the individual molecules or a different orientation of them becomes more stable. This leads to the existence of various *polymorphic phases* which are in general separated from each other by normal first-order transition points. Most organic substances show polymorphism; some of them possess even a considerable number of crystalline modifications which differ from each other only by rather small differences in the spatial arrangement of the individual molecules.

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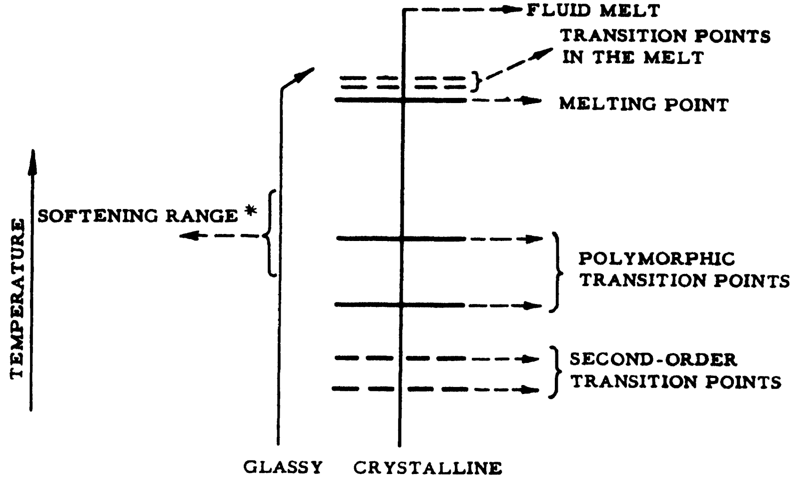
[4] Compare P. Ehrenfest, *Proc. Acad. Sci. Amsterdam*, **36**, 153 (1933); J. E. Mayer and S. F. Streeter, *J. Chem. Phys.*, **7**, 1019 (1939).

In general, it must be recognized that the solid state of organic substances is subject to many transition phenomena. These reflect the fact that the gradual consolidation of a three-dimensional lattice in which the individual units are of irregular shape and attract each other by a variety of relatively weak forces is a complicated multistep process of settling down to an ultimate arrangement of highest consolidation through a series of states of intermediate stability. Similarly, complicated conditions have also been found to prevail within a certain temperature range *above* the melting point, particularly if the individual molecules have a ribbonlike shape and exhibit polar attraction perpendicular to the axis and plane of the ribbon. In such cases, the crystals do not melt to a clear, homogeneous (Newtonian) liquid but are transformed into an opaque mass with characteristic optical and rheological properties, which is converted into a normal liquid only at temperatures noticeably above the "melting point." This existence of *liquid crystals* or *mesophases* is interpreted as indicating the presence of molecular aggregates or agglomerations in the melt inside of which there still exist certain restrictions in the free motion of the individual molecules. These aggregates have no permanent existence, but are of transient size and shape; they disappear and re-form more or less rapidly and cause the peculiar optical and rheological properties of the melt until—at sufficiently high temperatures—they degenerate into the random molecular structure of a normal liquid.

All these phenomena demonstrate that even for ordinary organic substances phase changes in the condensed state are by no means simple. They become particularly involved if the molecules have a shape—chains, ribbons, disks—departing widely from spherical symmetry and if the intermolecular forces are anisotropic. The influence of temperature on the gradual consolidation of such compounds is represented by a series of transition points from the clear fluid high-temperature melt to the last low-temperature crystalline modification. Among these transitions the "ordinary" melting point can lose much of the dominating character which it has in simpler cases. Yet all these phase changes are still in principle *equilibrium phenomena* which can be reproduced reversibly and exhibit the same characteristics regardless of whether one approaches the critical point from higher or lower temperatures.

It has, however, been found that *rate phenomena* also affect the melting and freezing of organic substances in a spectacular manner, particularly if the individual molecules are not too small and if hydrogen bonds are the reponderant lattice-forming forces. If a melt of such character is cooled, he individual molecules form strong bonds with each other before they ave time to assume the relative geometric arrangement which is required or the formation of the densest three-dimensional lattice—the melt beomes *supercooled,* and instead of a crystal there results a *glass.* This endency for supercooling is very common with organic substances and can n certain cases, such as glycerol or hexitol, go so far that it becomes exremely difficult to obtain any crystals of such substances at all.


FLUID MELT
TRANSITION POINTS IN THE MELT
MELTING POINT
TEMPERATURE
SOFTENING RANGE *
POLYMORPHIC TRANSITION POINTS
SECOND-ORDER TRANSITION POINTS
GLASSY
CRYSTALLINE

* Often above the transition points of crystalline modification.

Fig. 1. Transition points in glassy and crystalline materials.

The glassy state of organic substances is in general less stable than the orresponding crystalline state at the same temperature, but the drift oward equilibrium can be very slow whenever the viscosity of the glass is igh. Glasses of all kind—inorganic and organic—exhibit characteristic ransition phenomena in that within a relatively narrow temperature range ertain properties, such as specific volume, heat capacity, refractive index, iscosity, or modulus of elasticity, undergo relatively sharp changes. Vhether these transitions in the amorphous state are true equilibrium henomena such as those enumerated before (first- and second-order ransition points) is not yet perfectly understood; some of them such as the *oftening ranges* and *brittle points* seem to be clearly subject to rate processes, asmuch as the tests with the aid of which they are defined and established efer to the *rate* of flow or of deformation of the investigated sample.

To summarize schematically the discussion so far, attention is drawn to

Figure 1, which lists for the molten, crystalline, and glassy state of an ordinary organic substance the kind of transition phenomena one is likely to encounter.

2. Some Fundamental Aspects of the Texture of Organic Polymers[5]

The preceding discussion makes it evident that even ordinary low molecular weight organic compounds exhibit many and complicated transition phenomena in the condensed state; it will not therefore be surprising that with organic macromolecules one meets with correspondingly more involved conditions. The reasons for additional complications are manifold; only three of them will be discussed in some detail.

(a) SIZE OF PHASES

In ordinary low molecular weight substances the *phases* are always *large* as compared with the *individual molecules;* each crystal and each droplet of the melt is made up of a very large number (about 10^{14}) of independent molecules each of which—at a given instant—belongs either to the solid or to the liquid phase. In equilibrium—at the melting point—the *molecules are distributed among the coexisting phases;* they change rapidly their membership but never belong at the same time to both phases.

In a crystalline truly macromolecular material the *individual polymer molecules* are, at least in the direction of their maximum extension, *considerably larger* than the *individual phases.* In a fiber of hemp or flax the length of a crystalline domain is of the order of magnitude of 10^3 A., whereas the extended length of the macromolecules having a degree of polymerization of about 3000 is around 15×10^3 A.

The disordered domains are, on the average, probably shorter than the crystalline areas and, as a consequence, a single macromolecule passes through 15 to 20 different microphases and therefore belongs *at the same time* to several ordered and disordered volume elements. Here the *phases are distributed among the molecules,* and in the swollen state or close to the melting point the phases form and disappear along the individual macromolecules. A certain volume element, that is formed by a number of parallel individual chains, assumes by Brownian motion of the segments a high degree of lateral order for a certain period, then loses it again; after a while, another laterally ordered domain forms in its neighborhood and disappears in turn. This exchange of order along and among the macromolecules gives rise to an *average degree of order* in the sample which is characteristic for the given material at the given temperature and a given temperature and a given degree of swelling.

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[5] Compare R. F. Boyer and R. S. Spencer in *Advances in Colloid Science,* Vol. 2, Interscience, New York-London, 1946, p. 1; also T. Alfrey, Jr., *Mechanical Behavior of High Polymers,* Interscience, New York-London, 1948, p. 75; S. Krimm and A V. Tobolsky, *Textile Research J.,* 21, 805 (1951).

(b) INTERDEPENDENCE OF PHASES

In the normal treatment of phase equilibria and of the kinetics of phase formation, it is customary to neglect surface forces and to use thermodynamic functions which refer only to volume elements. The individual crystals of benzene which are in equilibrium with liquid benzene at the melting point can safely be considered to be *statistically independent* of each other; if one of them melts or grows, the others in its neighborhood are only affected in terms of a higher order approximation. In a partly crystalline polymer, the situation is entirely different; because the phases are "threaded up" along the macromolecules, changes at one part of a molecule will strongly influence its behavior at another part.

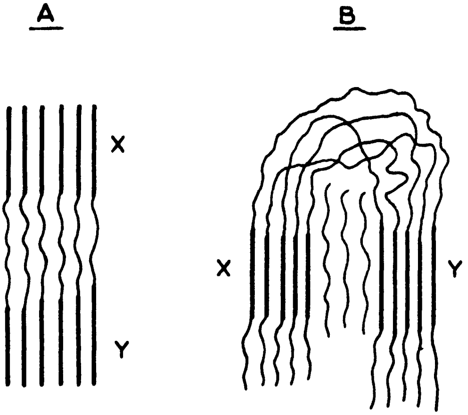

Fig. 2. Influence of crystalline regions on further crystal growth.

Two cases of this kind of *interdependence* of the individual microphases are represented schematically in Figure 2. In Figure 2A, two "crystals" are sketched which are behind each other and are connected by an amorphous domain in such a manner that all three phases are formed by the same macromolecules. If "crystal X" grows, it will compress segments of the throughgoing chains in a more random way in the amorphous domain and increase its entropy; this makes it more difficult for "crystal Y" to grow into the same amorphous area. In Figure 2B two "crystals" are sketched which are arranged parallel to each other connected with some of their chains and separated by an amorphous domain. If "crystal X" grows, the chains on its right side will be straightened out and will produce a tendency for additional crystallization of "crystal Y" parallel to "crystal X."

These two simple and grossly oversimplified cases show how the throughgoing macromolecules create a strong interdependence of neighboring ordered or disordered volume elements; phase changes at one point exert a profound influence on the environment. The spontaneous elongation on deswelling or cooling of prestretched fibers and the formation of spherulites in quenched bulk polymers are probably consequences of this coherence between the individual microphases.

(c) EFFECT OF EXTERNAL CONSTRAINTS

Phase transitions of ordinary substances are affected by the change of external parameters such as pressure or tension but the influence is comparatively small. The effect is related to the volume expansion or contraction which the material exhibits during the transition and amounts usually to a shift in the melting point of a few hundredths of one degree per atmosphere. Polymers behave quite differently. The melting point of the crystalline areas in relaxed Hevea rubber is about 20°C., whereas it is as high as 60°C. if the rubber is stretched to its fivefold length. The reasons for this difference are the filiform shape and the high internal flexibility of the individual macromolecules which lead to a much larger difference of the entropies of the material in the extended and relaxed state than can ever exist in an ordinary substance consisting of small essentially rigid and compact molecules.

This preponderant influence of entropy also is responsible for the existence of *rubberlike elasticity;* that is, the low-modulus, long-range, reversible extensibility of all polymeric substances, which are built up by long flexible macromolecules and which are tied into a three-dimensional network with the aid of distantly spaced cross-links. If a volume element containing such entangled networks is elongated in a certain direction, the flexibility of the relatively long chain segments between the cross-links readily permits a high degree of deformation without appreciable changes in internal energy but with considerable decrease in entropy. Only at higher elongations, when the individual chains of the network are sufficiently aligned and parallelized to permit lateral order to be easily established, does "crystallization" set in and is latent heat evolved.

The ordered domains formed in this way, however, differ in many respects from the well-known crystals of an ordinary organic substance. They have no plane faces and sharp edges; they are not independent of each other but cohere strongly by the amorphous matrix in which they are embedded. It is to a certain extent a mode of expression whether one prefers to say "crystalline domains are embedded in a disordered matrix" or "an orientated and laterally ordered system of parallelized macromolecules is interrupted by a number of lattice distortions." Figure 3 shows a number of chains arranged essentially parallel to each other in such a way that the total degree of molecular order is the same in Figure 3A and Figure 3B. The fact that the *disordered phase* is *coherent* in Figure 3A might induce one to use the words "amorphous matrix," whereas, for Figure 3B, where the *laterally ordered phase* is *coherent*, one might be compelled to prefer the expression "lattice distortions." It is very doubtful whether there exists at present any experimental method to distinguish between the cases of Figures 3A and 3B, if indeed there were any such distinction conceivable.

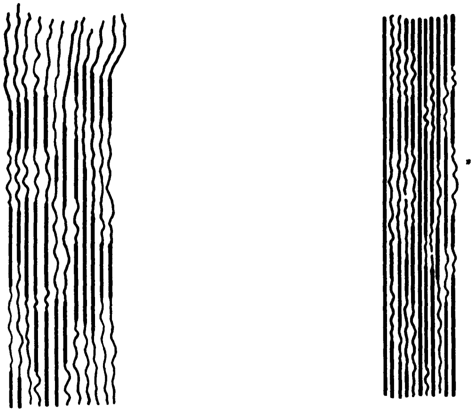
(*A*) (*B*)

Fig 3. Extreme manner of arrangement of amorphous and crystalline materials: (A) islands of ordered material embedded in a disordered matrix; (B) islands of disordered material embedded in an ordered matrix.

3. Phase Transitions in Organic High Polymers[6]

The general information presented under the two preceding topics makes it probable that relatively simple conditions can be expected to prevail only in completely amorphous and completely crystalline polymers. It is, however, doubtful whether truly macromolecular materials exist in either of these two extreme conditions. To the best of our present experimental knowledge, even very highly oriented filaments of cellulose, rubber, polyamides, and polyethylene still contain substantial amounts of disordered constituents. The estimates of the "degree of crystallinity" vary with the individual observer and experimental method he uses, but they never attain 100% and indicate that one always has to consider the existence of a certain amount of disordered domains left in a polymeric fiber, film, or test piece. As far as the completely amorphous state is concerned, it may appear at first sight that a polymer melt in its liquid and quenched state is entirely disordered. Unstretched Hevea rubber, neoprene or GR-S, and cast polystyrene or polymethylacetate exhibit x-ray diagrams which resemble very closely those of ordinary liquids and do not indicate the existence of large and well-developed laterally ordered domains. The rate of crystallization on stretching and other optical and rheological phenomena of these polymers, however, show the existence of very small areas with a certain degree of lateral order or at least of strong lateral attachments, so that a polymeric material in its molten or quenched state must be compared with a system of liquid crystals or of mesophases rather than with a normal Newtonian liquid. In fact, transition phenomena have been observed in polymer melts which resemble those known in the study of liquid crystals and mesophases.

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[6] Compare W. E. Roseveare, R. C. Waller, and J. N. Wilson, *Textile Research J.*, **18**, 114 (1948); K. Ward, Jr., *Textile Research J.*, **20**, 363 (1950).

As a consequence, we have to expect that a polymeric sample in its solid or semisolid (swollen) state will exhibit transition phenomena characteristic not only for the crystalline but also for the glassy state and will respond to mechanical deformations at various temperatures and in various conditions of swelling in a rather complicated manner. In principle, all transition temperatures and phase changes indicated in Figure 2 will be apt to occur simultaneously, although each of them will not affect the whole sample but only certain very small volume elements of it. Hence the behavior of the material will depend not only on the character of these individual volume elements—higher or lower degree of lateral order—and on their relative frequency in the system, but also on their geometric orientation and on the way in which they are distributed throughout the sample.

Natural fibers, such as cotton, hemp, flax, and wool, are known to possess a distinct morphology which profoundly influences their properties. Similarly, artificial fibers often exhibit a characteristic gross structure in which a more or less distinct skin–core relationship can be distinguished.

This has a noticeable influence on such important qualities as crimp, stiffness, recovery, and resistance against abrasion or fatigue under the combined influence of a constant and periodically varying stress or shear. Films cast from polymer melts or solutions often show the effect of "case hardening" in the form of more highly oriented and less laterally ordered surface layers and a less oriented but more crystalline bulk which affects such properties as luster, transparency, slip, heat-sealing, and limpness. Injection-molded or compression-molded test pieces of larger cross sections and irregular shape, such as combs, bottles, tubes, or supports and inserts for high-frequency electrical applications, show pronounced differences in density, orientation, and crystallinity in different parts of their various cross sections which influence impact strength, mechanical and electrical fatigue, crazing, and sensitivity against the attack of oxygen, solvents, and chemical reagents.

It can be anticipated and has, in fact, been demonstrated by our accumulated experimental knowledge that the influence of all factors enumerated above on the ultimate behavior of polymers is rather complex and specific in each individual case. As far as cellulose and its derivatives are concerned, these correlations will be discussed in more detail in the following sections of this chapter. It seems, however, that there exist a few relationships of a more general and fundamental character, which it will be worth while to summarize at the end of this introductory Section A to Chapter IV, although it must not be ignored that they lead only to approximate and sometimes oversimplified conclusions.

4. Influence of Phase Relations on Properties in Bulk Polymers

It appears that in a given test piece the crystalline domains are mainly responsible for its high resistance against swelling and softening and for its rigidity and density, whereas the laterally less ordered areas contribute softness, flexibility, and reversible extensibility. On the basis of this observation, a desirable material could be said to be one in which, at the same time, the crystalline domains possess a *high melting point* and the amorphous areas have a *low so-called second-order transition temperature.* If, in a sample of such nature, the "crystalline" and "amorphous" regions form interpenetrating three-dimensional networks, the ultimate macroscopic yielding of the material with increasing temperature will be controlled by the high-melting laterally ordered domains, whereas its final stiffening and embrittlement at low temperatures will be a matter of segment mobility in the disordered areas. One might consider the "crystals" to act as a high-softening *reinforcing filler* for the amorphous system, which in turn *plasticizes* the crystalline matrix in the domain of lower temperatures. In order that this beneficial interaction take place, it is necessary however that the two different phases be very finely distributed and intimately mixed. If, in a fiber, a highly crystalline skin were only loosely connected with an amorphous core, the specimen would not show an advantageous cooperation of its two phases; it would collapse at the softening point of the laterally disordered core and crack on bending, even at relatively high temperatures. Whenever a combination of desirable properties over a wider temperature range is needed, it appears that a fine grain is of decided advantage.

5. Factors Influencing Ease of Crystallization

In view of the importance of the total amount of the laterally ordered phase and of the characteristics of its distribution in the sample, the tendency of a given polymer to crystallize becomes a matter for thorough consideration. Although the exact formulation of this tendency is a complex problem, it seems that a few factors are of preponderant influence.[7]

(a) RIGIDITY OF CHAINS

Macromolecules having relatively rigid and inflexible chains crystallize more easily than those with chains of a high degree of internal flexibility. The rigidity can be caused by rigid chain links, such as the anhydroglucose rings in cellulose or the benzene rings in Terylene, Dacron, and Mylar or by the frequent appearance of substituents, such as in Teflon and Kel-F.[8]

(b) NATURE OF GROUPS IN CHAINS

If strongly polar groups or easily polarizable areas or hydrogen-bonding systems are regularly distributed along the length of the individual macromolecules, such as the OH groups in cellulose and polyvinyl alcohol or the —CO—NH— groups in polyamides and polypeptides, a distinct tendency for the formation of laterally ordered domains is produced. The closer the groups and the better their lateral fit, the more pronounced is their effect on crystallinity.[9]

[7] Compare L. A. Wood in *Advances in Colloid Science*, Vol. 2, Interscience, New York-London, 1946, p. 57.

[8] H. Mark, *Ind. Eng. Chem.*, **34**, 449, 1343 (1942); R. Hill and E. E. Walker, *J. Polymer Research*, **3**, 609 (1948).

[9] C. S. Fuller, W. O. Baker, and N. R. Pape, *J. Am. Chem. Soc.*, **62**, 3275 (1940); C. S. Fuller, C. J. Frosch, and N. R. Pape, *J. Am. Chem. Soc.*, **62**, 1905 (1940); **64**, 154 (1942).

(c) PERFECTION OF FIT

Bulky, nonpolar, and irregularly distributed substituents, which space the individual chain molecules apart from each other and prevent the establishment of hydrogen bridges, noticeably decrease the tendency for crystallination. The same effect is produced by the existence of asymmetrically substituted carbon atoms which permit the existence of D- and L-configurations in random sequences along the length of the individual macromolecules. The symmetry in the arrangement of the individual substituents along the chain appears to be of importance; symmetrical substitution, such as in Saran and polyisobutylene, favors crystallinity as compared with the less symmetric arrangement of the substituents in polyvinyl chloride and polypropylene. Copolymerization, in general, decreases the tendency for crystallization and, if carried out between monomers which form typically crystalline polymers, leads to phenomena similar to the eutectic behavior in metallic alloys.

There is, in fact, a striking similarity in the phase transitions of bulk polymers and of metallic systems with the reservation that the conditions enumerated under topic 2 have to be considered as producing important differences between these two classes of materials.

6. Crystallinity of Cellulose

Cellulose and its various derivatives were among the first polymers for which phase transitions in the solid and semisolid state were studied. Many concepts and ideas presented here were gradually developed by experimental data collected with cellulosic materials, and the prosecution of this approach still represents an important branch in cellulose research. The fine structure of the crystalline domains in cellulose I and II is relatively well known, but the proper characterization of the amorphous and glassy areas is still in a rather preliminary state and suffers from the lack of adequate experimental methods.

As compared with other polymers, cellulose shows a distinct tendency for crystallization, probably caused by the relative stiffness of the glucosidic chains and the hydrogen-bonding capacity of its frequent hydroxyl groups. The flat shape of the rings and the spatial distribution of the hydroxyl groups appear to favor the formation of ribbon-shaped laterally ordered sheets which exhibit a threefold anisotropy as far as bonding strength is concerned.[10]

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[10] Compare P. H. Hermans, *Physics and Chemistry of Cellulose Fibres*, Elsevier, New York, 1949, p. 399· also O. Kratky, *Chemische Textilfasern*, Encke, Stuttgart, 1951.

Along the macromolecules, in the direction of the *b*-axis of the crystalline domains, the coherence is affected by covalent 1,4-glucosidic bonds between carbon and oxygen atoms, which have a dissociation energy of about 80 kcal. Perpendicular to the chains, in the planes of the anhydroglucose rings and in the direction of the *a*-axis of the lattice, the hydrogen bonds between the hydroxyl groups and the ring oxygen atoms are responsible for the coherence; they have an average bond strength of around 5 kcal. Finally, perpendicular to the chains and to the plane of the anhydroglucose rings and parallel to the *c*-axis of the lattice, the only existing attraction is due to van der Waals forces between the anhydroglucose rings and their substituents which can be calculated to be 2–3 kcal. per mole.

This system of bonding can be considered as a reasonable starting point for the explanation of the crystallization tendency of cellulose. It leads to the existence of elongated thin sheets with high lateral order, which in turn seems to explain in a satisfactory way the observed macroscopic mechanical and flow properties of cellulose fibers and films in the dry and swollen state.

B. SUBMICROSCOPIC STRUCTURE

JOHN A. HOWSMON AND WAYNE A. SISSON

Because of the abundance of cellulose in nature and its importance to man in textile and other applications, the structure and properties of cellulose have been studied more thoroughly than those of any other polymeric system. In many cases, these investigations antedate the development of polymer theory and practice to such an extent that for several years theories of polymer structure were for the most part cellulose structure theories. In other cases, these investigations were instrumental in advancing experimental techniques which have proved to be invaluable in general polymer evaluation. For example, cellulose was the first organic high polymer to be subjected to a thorough analysis by x-ray diffraction,[1] and since its various forms exhibited x-ray diagrams ranging from poor to excellent, rapid advances in experimental techniques for fiber diagrams and their theoretical evaluation resulted. Rapid advances since about 1925 in the fields of physics and chemistry of high polymers have welded many of these early theories for cellulose and other natural polymers into generally accepted theories of polymer structure which seem to be universally applicable to both natural and synthetic products. During this time it has become evident that the nature of the monomer, the way in which the monomers are linked together into the molecule, and the ways in which the molecules pack in the solid state determine, to a great extent, the physical and chemical behavior of high polymers.

Most high polymers, under proper conditions, will crystallize to form imperfectly ordered solids which exhibit a complex polyphase structure. Certain regions within a given sample possess a high degree of internal geometrical order and are commonly called "crystallites." These regions have many properties found in crystals of low molecular weight compounds; they diffract x-rays to produce regular fiber diagrams and they exhibit birefringence. Unlike crystals of low molecular weight materials, however, these regions do not have well-defined plane boundaries or sharp edges. Their size and/or degree of perfection seem to vary widely from sample to sample or even in different parts of a given sample, and almost without exception they are rodlike or ribbonlike. These "crystallites" seem most comparable to the grains of a polycrystalline metal.[2]

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[1] Compare K. H. Meyer and H. Mark, *Der Aufbau der hochpolymeren organischen Naturstoffe*, Akadem. Verlagsgesellschaft, Leipzig, 1930, pp. 94 ff.; H. Mark, *Physik und Chemie der Zellulose*, J. Springer, Berlin, 1932, pp. 126–176.

High polymers do not consist entirely of such crystalline domains, but always contain a certain number of disordered, entangled chain molecules which give rise to "amorphous" or "disordered" regions. Like the crystallized regions, these disordered portions may also vary in size and/or degree of imperfection or randomness in different polymers or within a given polymer sample.

For a given set of conditions of temperature and stress, the extent to which crystallized and disordered portions are present in a given sample of material is dependent upon the geometric fitting of the molecules into a crystal lattice. This concept has been discussed by Mark and Tobolsky[3] and may be summarized as follows:

(1) If the intermolecular attraction is weak and the chain molecules are difficult to fit laterally into a lattice structure, the molecules will show a distinct tendency to return to a curled, relaxed state and the material is a typical rubber.

(2) If the intermolecular attraction is strong and the chain molecules are easily fitted laterally into a crystal lattice, a state of high crystallinity is favored and the material is a typical fiber.

(3) If the intermolecular attraction is moderate and the molecular geometry is reasonably favorable for crystallization, the polymer behavior will depend greatly upon external conditions and the material is a typical plastic.

(4) Other conflicting combinations of intermolecular attraction and molecular geometry may result in borderline cases. For example, molecules such as polyethylene that will fit easily into a crystal lattice will crystallize under the influence of comparatively weak interchain forces and tend to be more fiberlike than would be expected from consideration of intermolecular forces alone. Conversely, materials consisting of bulky or irregular chains, such as mixed cellulose esters, will not crystallize readily even though the intermolecular forces are very strong. In these cases a tendency toward

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[2] Compare C. S. Barrett, *Structure of Metals*, McGraw-Hill, New York, 1943, pp. 154–158, 381–385.

[3] H. Mark and A. V. Tobolsky, *Physical Chemistry of High Polymeric Systems* (High Polymers, Vol. II), 2d ed., Interscience, New York-London, 1950, pp. 146–151.

rubberlike behavior is evident at temperatures above the softening or second-order transition point.

These qualitative considerations indicate that the differences among rubbers, fibers, and plastics are not intrinsic but are a matter of degree in the extent to which crystallized and disordered regions appear in a given sample. Cellulose fits this qualitative scheme very well; it has a relatively inflexible chain, strong intermolecular forces, and a highly symmetrical configuration easily fitted into a crystal lattice. All these factors should favor a high crystallinity.

The crystallinity of cellulose was first confirmed by Nishikawa and Ono[4] who showed that the x-ray diagram consisted of definite diffraction rings. That this crystallinity was discontinuous was first postulated by Nishikawa[5] who reasoned that any material which gave a fiber diagram must be a polycrystalline aggregate in which the crystals are arranged parallel to the fiber axis. This dual structure of discontinuous crystallinity in which the crystals are separated by more or less disordered material, coupled with the usual orientation of the crystallized areas in respect to some sample dimensions, is one of the most characteristic features of fibers and is known as fiber structure.

In order to characterize such a complex structure completely, it is necessary to consider: (1) the spatial arrangement of the atoms within the molecules; (2) the spatial arrangement of the molecules within the crystalline portion; (3) the size and shape of these crystalline portions; (4) the relative amounts of the so-called "crystalline" and "amorphous" phases; (5) the orientation of the crystalline and amorphous phases with respect to one another and to the fiber surfaces.

It is desirable to divide the information concerning these factors into two types depending upon whether or not the fiber has been treated with any of a number of chemical reagents. The data will therefore be presented under two headings: "Cellulose Fiber Structure" which will treat the fine structure of untreated native and regenerated cellulose fibers, and "Cellulose Fiber Reactions" which will treat the fine structure of cellulose derivatives and the changes in structure which accompany chemical treatments of cellulose fibers.

1. Cellulose Fiber Structure

Our present knowledge regarding the submicroscopic or fine structure of cellulose has been contributed by a large number of workers over a period of many years. Detailed surveys of most of the early work have been published elsewhere,[6,7] and comprehensive discussion of this work cannot be repeated here. Brief summaries of the early investigations will be made when needed as background or as an integral part of our present theories. The discussion of structure will be divided into four sections: (a) crystalline structure which is described in terms of molecular configuration and unit cell arrangement; (b) amorphous structure; (c) crystalline–amorphous multiphase structure and its variations; and (d) orientation.

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[4] S. Nishikawa and S. Ono, *Proc. Math.-Phys. Soc. Tokyo,* **7,** 131 (1913).

[5] S. Nishikawa, *Proc. Math.-Phys. Soc. Tokyo,* **7,** 296 (1914).

(a) CRYSTALLINE STRUCTURE

In studying the structure of low molecular weight organic compounds which form large single crystals, it is usually possible to determine both the crystallographic unit cell and the positions of the atoms within the molecule by x-ray diffraction methods. However, in the case of complex materials such as cellulose which do not form macrocrystals, definite atomic configurations cannot be obtained from x-ray evidence and therefore approximations must be made from combined x-ray and stereochemical evidence. In the first spatial model of the cellulose molecule as depicted by Sponsler and Dore,[8] the glucose residues were assumed to be linked alternately by 1,1-glucosidic and 4,4-etherlike bonds.

For reasons of symmetry the beta structure was given preference to the alpha structure. This structure was not in agreement with the chemical evidence of Haworth[9] for the alternating 1,1- and 4,4- linkages did not provide an explanation for the formation of cellobiose on hydrolysis. Therefore, Haworth suggested that the alternating 1,1-, 4,4- system be replaced by 1,4-, 1,4- linkages and proposed another model which had to be rejected because the assumed distance of 1.5 A. between carbon atoms 6 and 2 of neighboring rings was irreconcilable with known interatomic distances.

In an effort to reconcile the x-ray and chemical evidence, work was undertaken by Meyer in conjunction with Mark, and in 1928 Meyer and Mark[10,11] showed that a model could be constructed which was in agreement with both x-ray and chemical data. Using 1.54 A. as the distance

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[6] W. A. Sisson in E Ott, ed., *Cellulose and Cellulose Derivatives* (High Polymers, Vol. V), Interscience, New York-London, 1943, pp. 203–285.

[7] P. H. Hermans, *Physics and Chemistry of Cellulose Fibres*, Elsevier, New York, 1949.

[8] O. L. Sponsler and W. H. Dore, in *Colloid Symposium Monograph*, Vol. IV, Chemical Catalog Co., New York, 1926, p. 174.

[9] W. N. Haworth, *Helv. Chim. Acta*, **11**, 547 (1928).

[10] K. H. Meyer and H. Mark, *Ber.*, **61B**, 593 (1928).

[11] K. H. Meyer, *Z. angew. Chem.*, **41**, 935 (1928).

between carbon atoms, 1.35 A. as the distance between carbon and oxygen atoms, and the beta form of Haworth's cellobiose formula, this model is most simply depicted as shown in Figure 4. In accordance with x-ray fiber diagrams which demand a diagonal screw axis with a repeat pattern every 10.3 A., the length of this unit is 10.3 A.; the fact that the lower half of the unit is turned through 180° fulfills the screw axis requirement and allows the 1,4- linkage required by chemical evidence. Thus, the chains are very nearly straight and the planes of the two anhydroglucose units deviate only slightly from the plane of the paper. Cellulose molecules which are not associated in crystallite formation need not retain this extended form for although the glucose ring framework is fairly rigid, rotation around the oxygen bridge between anhydroglucose units is possible. However, at least four different crystalline modifications which possess this extended form have been reported.

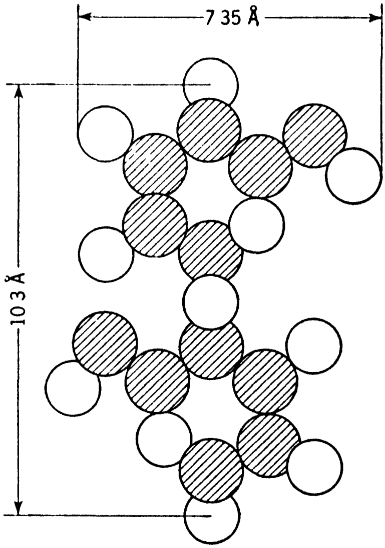

Fig. 4. Cellobiose unit according to Haworth (Meyer and Mark[12]). Carbon atoms are represented by shaded circles; oxygen atoms by open circles; hydrogen atoms are not shown.

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[12] K. H. Meyer and H. Mark, *Der Aufbau der hochpolymeren organischen Naturstoffe*, Akadem. Verlagsgesellschaft. Leipzig. 1930. p. 110.

(1) *Crystalline Structure of Cellulose I*

As early as 1920, Herzog and Jancke[13] recognized that cellulose from such widely different sources as cotton, ramie, wood, jute, and flax gave identical x-ray diagrams and concluded that all these fibers had identical crystalline structures. Later work has shown that this identity extends to all other natural cellulosic materials including bacterial and animal cellulose with the possible exception of the marine plant *Halicystis*.[14] This crystal form has become commonly known as the "native" cellulose form, but the more general term "cellulose I" is now preferred.

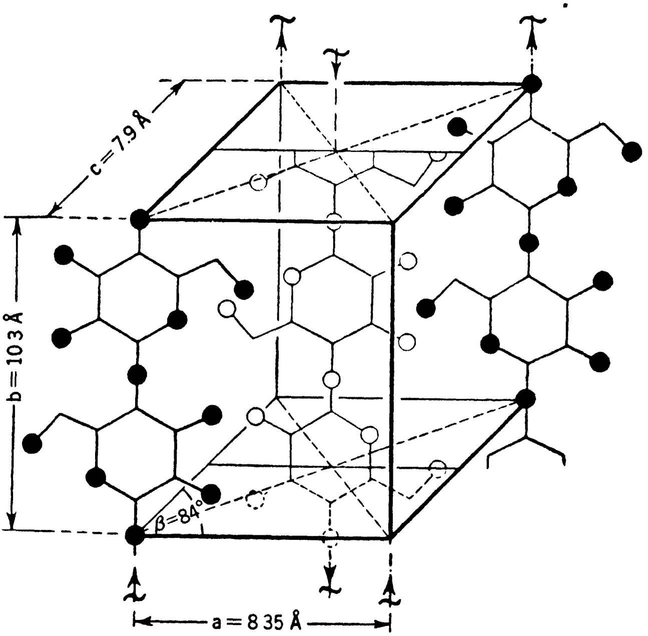

Fig. 5. Unit cell of cellulose I (Meyer and coworkers[17-19]).

The first unit cell dimensions to be accepted by later investigators were calculated by Polanyi[15] who postulated a rhombic unit cell with dimensions 7.9 × 8.45 × 10.2 A. In 1926, Sponsler[16] attacked the same problem and postulated an orthorhombic unit cell with the dimensions 6.10 × 5.40 ×

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[13] R. O. Herzog and W. Jancke, *Z. Physik*, **3**, 196 (1920).

[14] W. A. Sisson, *Science*, **87**, 350 (1938).

[15] M. Polanyi, *Naturwissenschaften*, **9**, 288 (1921).

[16] O. L. Sponsler, *J. Gen. Physiol.*, **9**, 677 (1926).

10.25 A. This latter contribution was of importance because it first pointed out that the unit cell as deduced from x-ray data was much smaller than the cellulose molecule.

A series of investigations by Meyer and coworkers[17–19] then led to the postulation of a monoclinic unit cell as shown in Figure 5 with axes: a = 8.35 A.; b = 10.3 A. (fiber period); c = 7.9 A.; β = 84°. The unit cell most probably belongs to space group P2, and contains four glucose residues. This structure was confirmed by Gross and Clark[20] and is still generally accepted. The planes of the glucose units (now usually called anhydroglucose unit or glucopyranose unit) lie in the *ab* plane and the axes of the cellobiose units are parallel to the *b* axis of the unit cell. By referring to Figure 5 it can be seen that the unit cell is composed of two sets of chains each having a twofold screw axis parallel to the *b* axis of the cell and that the set of chains running through the *ac* face is displaced along the *b* axis so that one glucose unit occurs in the approximate center of the cell. Meyer and Mark[17] originally assumed these two sets of chains to run in the same direction, but Meyer and Misch[18,19] reasoned that the cellulose chains in a newly coagulated viscose should run in both directions and assumed the alternating orientation shown in Figure 5 by the arrows denoting chain direction. They found good agreement between the calculated x-ray intensities required by this model and the observed intensities. It should be pointed out however that this alternating orientation is merely assumed and that other possibilities such as the existence of random distribution of upward and downward chains in the lattice or the simultaneous presence in each fiber of crystallites in which all chains run upward and others in which all chains run downward cannot be excluded on the basis of existing data.[21]

Further information regarding the nature of forces which hold the lattice structure together has been reviewed by Mark.[22] In the direction of the *b* axis the glucose units are held together by strong 1,4-glucosidic primary valence bonds. Along the *a* axis the glucose rings are separated by only 2.5 A. This suggests that relatively strong forces are acting in this plane, and it is reasonable to assume that hydrogen bonds are formed between oxygen atoms of adjacent molecules. Along the *c* axis the nearest distance between atomic centers is 3.1 A. which corresponds closely to the distance expected if van der Waals forces hold the lattice together in this direction. Thus, cellulose may be regarded as a combination of a chain lattice and a layer lattice composed of primary valence forces along the *b* axis, relatively strong hydrogen bond network in the *ab* plane, and weaker van der Waals forces perpendicular to the *ab* plane. These three different forces acting in three different directions may be responsible in part for many of the properties of cellulose in the solid state.

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[17] K. H. Meyer and H. Mark, *Z. physik. Chem.*, **B2**, 115 (1929).

[18] K. H. Meyer and L. Misch, *Ber.*, **70B**, 266 (1937).

[19] K. H. Meyer and L. Misch, *Helv. Chim. Acta*, **20**, 232 (1937).

[20] S. T. Gross and G. L. Clark, *Z. Krist.*, **A99**, 357 (1938).

[21] A. J. A. van der Wyk and K. H. Meyer, *J. Polymer Sci.*, **2**, 583 (1947).

[22] H. Mark, *Chem. Revs.*, **26**, 169 (1940).

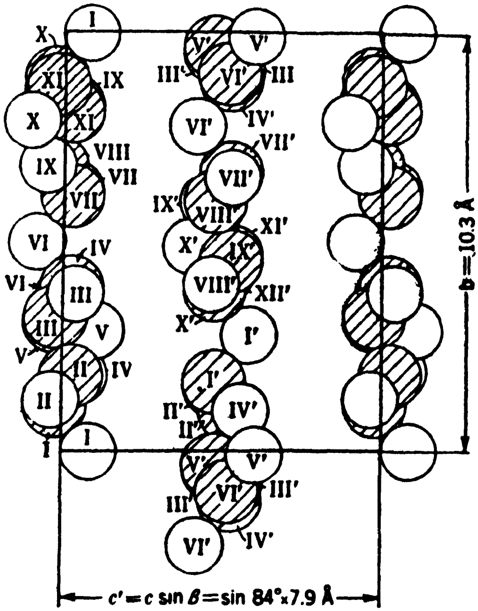


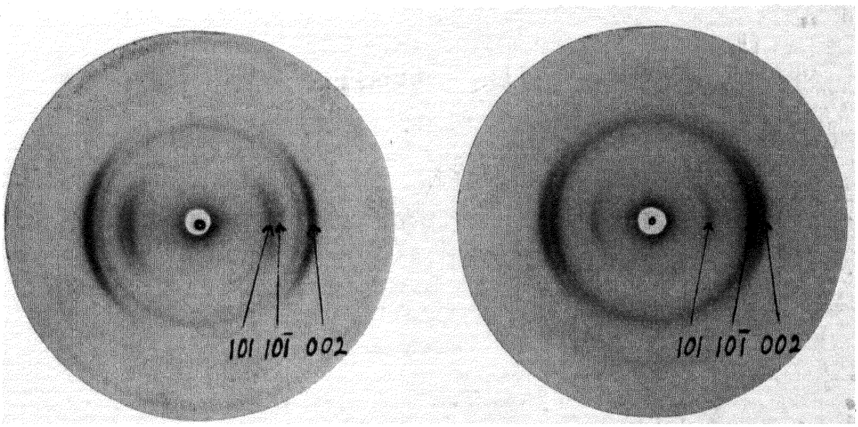
Fig. 6. Projection of the unit cell viewed along *a* on the plane *bc'* ⊥ *a* (Meyer and Misch[19]).

Although it is impossible to determine the exact position of each atom in this structural model, Meyer and Misch[19] have made calculations for a number of arrangements and found good agreement of the calculated and observed x-ray intensities for the configuration shown in Figure 6. The essentially linear molecular chains are built up by 1,4- linkages from anhydroglucose units in the armchair form. Though not exact, this configuration can be assumed to be a reasonable approximation of the actual arrangement.

This structure has been challenged on several occasions[23–26] usually on the basis of the appearance of x-ray reflections forbidden by the unit cell shown[27,28] or of calculated intensity discrepancies. These considerations have been reviewed by van der Wyk and Meyer[21] who conclude that most of the refinements in unit cell configuration suggested are unwarranted by specific data and that the cell shown in Figure 5 is in best agreement with experimental evidence. In any case, it should be remembered that because of the absence of single cellulose crystals the exact definition of the unit cell is impossible and that all such cells are approximations dependent upon lattice distortion in polycrystalline aggregates.

(2) *Crystalline Structure of Cellulose II*

If cellulose is dissolved and precipitated from solution or regenerated from some addition compound of cellulose I, such as alkali cellulose which is formed in mercerization, the molecules do not reassemble into the characteristic cellulose I lattice but into an allotropic modification. This



(A) (B)

Fig. 7. X-ray diagrams of cotton (A) before mercerization (cellulose I) and (B) after mercerization (cellulose II) showing location of 101, $10\bar{1}$, and 002 diffraction rings.

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[23] F. T. Pierce, *Trans. Faraday Soc.*, **42**, 545, 560 (1946).

[24] E. Sauter, *Z. physik. Chem.*, **B35**, 83 (1936); **B43**, 294 (1939).

[25] R. Hosemann, *Z. Elektrochem.*, **46**, 535 (1940).

[26] W. T. Astbury and M. M. Davies, *Nature*, **154**, 84 (1944).

[27] H. Kiessig, *Z. physik. Chem.*, **B43**, 79 (1939).

[28] K. H. Meyer and A. J. A. van der Wyk, *J. Polymer Sci.*, **1**, 46 (1946).

modification is known variously as "hydrate," "mercerized," or "regenerated" cellulose. However, since celluloses exhibiting this crystal form have the same composition as cellulose I, and since this form is very general for all rayons, cellophanes, and mercerized celluloses, it seems better to designate this form simply as cellulose II.

The representation of the lattice structure of cellulose II is usually based on the monoclinic unit cell found by Andress[29] with axes: a = 8.14 A.; b = 10.3 A.; c = 9.14 A.; β = 62°. Like cellulose I this unit cell most probably belongs to space group P2, and contains 4 anhydroglucose units· Typical x-ray diagrams of cellulose I and II are shown in Figure 7 and the corresponding unit cell structures are compared in Figure 8.

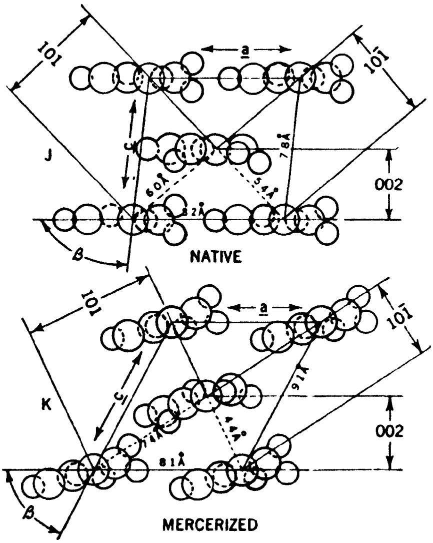

Fig. 8. View down b axis of unit cell of native (cellulose I) and mercerized (cellulose II) cellulose showing the location of a and c axes, angle β, and the (101), $(10\bar{1})$, and (002) planes (Andress[29]).

It may be assumed that along the fiber axis (perpendicular to the plane of the paper) the chains are arranged along a screw axis as in cellulose I. However in cellulose II, the molecules are displaced relative to one another along the a axis and rotated about 30° out of the ab plane. As a result the coherence of the ab layer is diminished, and new planes appear whose molecules are probably connected to one another by hydrogen bonds in the diagonal $(10\bar{1})$ plane.

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[29] K. R. Andress, *Z. physik. Chem.*, **34**, 190 (1929).

As in the case of cellulose I, a unit cell for this structure cannot be determined unequivocally and the problem cannot be considered solved. Other authors[23,24,30–32] have suggested other unit cells and possible refinements of the one given, but the Andress unit cell seems to be the best approximation at this time.

(3) *Cellulose III and Cellulose IV*

The decomposition of the swelling compound of cellulose with liquid ammonia, ammonia cellulose I, has been reported[33–37] to lead to the formation of various modifications of cellulose according to the conditions used. Among these modifications is one described as cellulose III whose x-ray diagram indicates that the plane of the anhydroglucose unit is markedly twisted out of the *ab* plane[33,36] in a fashion similar to that shown in Figure 8 for cellulose II. The x-ray diagram of this product is quite similar to that of cellulose II, and unit cell structures for cellulose III quite similar to those of cellulose II have been suggested by both Barry and coworkers[33] and Legrand.[37] According to Legrand the unit cell dimensions are: $a = 7.74$ A.; $b = 9.96$ A.; $c = 10.3$ A.; and the angle $\beta = 58°$. Hess and Gundermann[36] have proposed another unit cell. On the basis of present data it is impossible to establish any structure conclusively.

It was first shown by Meyer and Badenhuizen[38] and confirmed by Kubo and Kanamaru[39] that when highly stretched Lilienfeld rayon (cellulose II) is heated at temperatures between 140°C. and 300°C., in water under pressure, in glycerol, or in formamide, the crystal form is converted wholly or in part depending upon conditions into a modification which from x-ray diagrams appeared to be identical to cellulose I. However, later investigators[40–42] decided that this modification was not identical to cellulose I

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[30] K. H. Meyer and H. Mark, *Z. physik. Chem.*, **B36**, 232 (1937); **B38**, 395 (1938).

[31] O. L. Sponsler and W. H. Dore, *J. Am. Chem. Soc.*, **50**, 1940 (1928).

[32] A. Burgeni and O. Kratky, *Z. physik. Chem.*, **B4**, 401 (1929).

[33] A. J. Barry, F. C. Peterson, and A J. King, *J. Am Chem. Soc.*, **58**, 333 (1936).

[34] G. L. Clark and E. A. Parker, *J. Phys. Chem.*, **41**, 777 (1937).

[35] K. Hess and C. Trogus, *Ber.*, **68B**, 1986 (1935).

[36] K. Hess and J. Gundermann, *Ber.*, **70B**, 1788 (1937).

[37] C. Legrand, *J. Polymer Sci.*, **7**, 333 (1951).

[38] K. H. Meyer and N. P. Badenhuizen, *Nature*, **140**, 281 (1937).

[39] T. Kubo and K. Kanamaru, *Z. physik. Chem.*, **A182**, 341 (1938).

[40] K. Hutino and I. Sakurada, *Naturwissenschaften*, **28**, 577 (1940).

[41] T. Kubo, *Z. physik. Chem.*, **A187**, 297 (1940).

[42] K. Hess and H. Kiessig. *Z. physik. Chem.*, **B49**, 235 (1941).

and subsequently have referred to it as "high temperature" cellulose, cellulose T, and cellulose IV. The unit cell is described as rhombic with dimensions $a = 8.11$ A.; $b = 10.3$ A.; $c = 7.9$ A.; and the angle β approximately 90°. According to Kubo[41] the arrangement is quite similar to that of cellulose I except that the groups of chains are displaced relative to one another along the b axis.

The completeness of this transformation depends on the kind of fiber and on various other factors which have not been completely characterized. In general, for any condition the transformation is easier and/or more complete for regenerated fibers than for mercerized native fibers. This difference is ascribed to lower crystalline order in regenerated fibers, and hence lower energies are required. Dry rayon is practically unchanged at temperatures as high as 300°C., but practically complete transformation occurs in 30 min. in glycerol at 250°C. and partial transformation in 30 min. in water or formamide at 200°C. Thus water and other polar liquids facilitate the transformation. The effect of heating in the presence of a large number of materials has been studied by Kubo and Kanamaru[39] who found that the degree of transformation increases proportionally to the polarity of the liquid used. If rayon fibers are first swollen with sodium, potassium, or lithium hydroxide[41] or with a diamine,[43] the transformation is greatly facilitated, becoming almost complete on subsequent heating in glycerol. Hermans and Weidinger[44] have shown that almost complete transformation can be obtained with mercerized ramie by first swelling in water, replacing the water with glycerol, and heating to 250–275°C. In all these cases the difference in degree of transformation is ascribed to the separation of the cellulose molecules by the swelling agents which permits easier rotation of the anhydroglucose units back into the ab plane.

Partial transformation may result at lower temperatures as in the case of heating alkali cellulose in water at 100°C. or cellulose III in water at 200°C.[42] Small amounts of cellulose IV may also be formed during the spinning of rayon[45,46] under certain conditions or by direct decomposition of metal cellulose xanthates.[46] In these cases the partial formation of cellulose IV may occur at temperatures as low as 80°C. with almost complete transformation at temperatures in the range 100–150°C. Thus, it would seem that the formation of cellulose IV directly or from cellulose II is facilitated by any condition which lowers the "effective melting point" of the cellulose used.

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[43] T. Kubo, *Cellulose Ind.* (Tokyo), **15**, 99 (1939).

[44] P. H. Hermans and A. Weidinger, *J. Colloid Sci.*, **1**, 495 (1946).

[45] H. G. Ingersoll, *J. Applied Phys.*, **11**, 924 (1946).

[46] J. A. Howsmon, unpublished data.

(4) *Present Status of Polymorphy of Cellulose*

As previously pointed out, the exact definition of a crystal modification in a polycrystalline polymer such as cellulose by x-ray methods alone is virtually impossible because of complications arising from structure imperfections, and at this time there remains reasonable doubt that the four forms discussed are all stable polymorphic forms. Of the four, only two occur in nature: cellulose I, in the crystalline fraction of most natural fibers such as cotton, ramie, flax, hemp, and wood; and cellulose II, in the marine alga *Halicystis*.[14] These two forms apparently represent distinctly different structures.

Baker[47] has suggested that the complex literature on the structure of cellulose esters and other derivatives can be greatly simplified by a concept of a continuous range of states of local chain order rather than definite polymorphic forms and that true polymorphism has been confused with the incidence of unstable states. He points out that in many cases different polymorphic forms have been postulated principally on the basis of differences in sharpness and intensity of x-ray diffraction spots rather than on actual arrangement, and shows distinct evidence that these features and even the actual appearance of a given diffraction spot are critically dependent on the degree of molecular ordering in the sample. On this basis it is interesting to compare more closely the proposed structures of the four forms of cellulose. These forms are summarized in Table 1, in which a striking similarity between celluloses I and IV and between celluloses II and III can be noted. The principal x-ray evidence for distinct existence of cellulose IV lies in the fact that only one equatorial interference occurs in place of the 101, $10\bar{1}$ doublet of cellulose I (Fig. 7). Similarly in cellulose

TABLE 1

The Unit Cell Structures of Polymorphic Forms of Cellulose

Axis	Cellulose I	Cellulose IV	Cellulose II	Cellulose III
a	8.35 A.	8.11 A.	8.1 A.	7.74 A.
b	10.3 A.	10.3 A.	10.3 A.	10.3 A.
c	7.9 A.	7.9 A.	9.1 A.	9.9 A.
β	84°	90°	62°	58°

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[47] W. O. Baker, *Ind. Eng. Chem.*, **37**, 246 (1945).

III only one interference occurs in place of the $10\bar{1}$, 002 doublet in cellulose II. It is striking that in the above cases the single observed interference occurs in the x-ray diagram of cellulose IV between the expected positions of the 101 and $10\bar{1}$ spots of cellulose I and in the x-ray diagram of cellulose III between the expected positions of the $10\bar{1}$ and 002 spots of cellulose II. Such a condition could arise from disorder as proposed by Baker. The conditions necessary for conversion of cellulose II to the so-called cellulose IV usually cause ordering or crystallization to a greater extent than is normally found in the starting material. The final state after transformation, however, still represents a much lower level of order, as indicated by high moisture sorption and swelling,[46] than that found in the natural fibers from which the cellulose I structure is calculated. The possibility of unstable states is also indicated by the work of Legrand,[37] who reports that cellulose III made from mercerized fibers can be converted to cellulose II by the action of water.

It does not seem necessary on the basis of present evidence that cellulose III and cellulose IV be true polymorphic forms in the same sense that cellulose I and cellulose II are polymorphic. Without introducing any errors of consequence, cellulose IV can be regarded as a disordered form of cellulose I and cellulose III as a disordered state approximating cellulose II.

(5) *Effect of Crystalline Structure on Cellulose Properties*

It has been known almost from the discovery of the process of mercerization that marked changes in macroscopic properties such as moisture sorption, dye sorption, swelling, tenacity, and elongation accompany mercerization treatments or procedures involving solution and reprecipitation of cellulose. Then when x-ray evidence showed that these processes also completely changed the crystal form from that of cellulose I to that of cellulose II, there was a tendency to attribute a great significance to the effect of this transformation on the physical properties. However, as early as 1934, Katz[48] pointed out that natural fibers, which had been nitrated and then denitrated under such conditions that the cellulose I modification was retained, still exhibited the properties of mercerized fibers such as enhanced sorptive power and swelling. In his review of mercerization, Valko[49] has also reasoned that the changes in properties produced by mercerization are not due to the presence of cellulose II, but to decreases in the amount of crystalline material and changes in crystallite orientation which accompany mercerization.

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[48] J. R. Katz, *Die Röntgenspektrographie als Untersuchungsmethode*, Urban und Schwarzenberg, Berlin, 1934, p. 92.

[49] E. I. Valko, in E. Ott, ed., *Cellulose and Cellulose Derivatives* (High Polymers, Vol. V), Interscience, New York-London, 1943, pp. 324–340.

By varying the conditions of rayon spinning, it has been possible to spin rayon yarns containing varying amounts of both cellulose II and cellulose I (or IV) structures with either constant orientation and crystallization or constant orientation and varying crystallization.[46] In accord with previous conclusions, there was no apparent correlation between the cellulose I content of these fibers and either moisture sorption, tenacity, elongation, or swelling. However, both moisture sorption and swelling decreased rapidly with increasing crystallization regardless of the crystal form present. Hermans and Weidinger[50] have found evidence that the cellulose II crystal form may absorb water within the crystallite itself whereas the cellulose I crystal form will not. This is a property which may well affect others, but conclusive evidence that this property is a function only of crystalline modification and not possibly of disordered states is lacking. In any event it seems more correct to regard the various transformations from one crystal form to another as interesting but accessory phenomena, for none of the differences in important technological properties can be attributed solely to the differences between crystal forms.

(b) NATURE OF AMORPHOUS REGIONS

The so-called "amorphous" material present in polymers is usually defined and identified by its failure to produce definite x-ray diffraction lines and, as such, does not lend itself to most of the common methods of studying geometric order. However, in certain more or less ideal cases such as natural rubber which normally occurs as a completely "amorphous" polymer, it has long been known that the order within this state is quite analogous to that in a low molecular weight liquid and can be characterized by x-ray diffraction and thermodynamic properties. Moreover, as crystalline rubber is formed on stretching, very little change in the amorphous fraction other than a decrease in quantity occurs, and the polycrystalline rubber polymer consists essentially of reasonably perfect crystallites embedded in a uniform amorphous matrix.[51,52] With cellulose the case is not so simple and although direct evidence is lacking, indirect evidence supports the view that much larger variations in the amorphous regions from fiber to fiber occur in cellulose than are usual for rubberlike materials.

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[50] P. H. Hermans and A. Weidinger, *J. Colloid Sci.*, **1**, 185 (1946).

[51] E. A. Hauser and H. Mark, *Kolloidchem. Beihefte*, **22**, 63 (1926).

[52] S. D. Gehman and J. E. Field, *J. Applied Phys.*, **12**, 23 (1941).

Amorphous cellulose prepared by evaporation of ammonia from ammonia cellulose,[33] by denitration of cellulose nitrate,[53] and by dry grinding of cellulose in a vibratory ball mill[54,55] has been described and characterized by x-ray diffraction. As expected, these materials possess a liquidlike structure whose x-ray scattering curve contains one broad maximum similar to that for unstretched rubber. There is no evidence that this liquid-type structure is carried over into the polycrystalline cellulose fiber, and there appears to be no connection between this type of structure and the structure of amorphous regions in the untreated fiber. In fact most of these "amorphous" celluloses crystallize readily on wetting or even on exposure to water-saturated air. This highly amorphous structure, therefore, is very unstable and illustrates the strong crystallization tendency of cellulose to crystallize by hydrogen bonding. Such a structure will never appear in a cellulose fiber as a distinct phase over any large volume.

A crystalline region may be defined as a region in which a highly geometric order prevails with the distance between neighboring molecules governed by strict laws. An amorphous region on the other hand cannot be defined as one in which there is a complete lack of geometric order similar to that existing in the liquid state. An amorphous region, in the sense that the term is commonly used, must be considered to contain all possible intermediate degrees of packing between the liquid state and crystalline state.

(c) CRYSTALLINE-AMORPHOUS MULTIPHASE STRUCTURE

In a cellulose fiber the three-dimensional unit cell arrangement of cellobiose units is repeated in all directions to build up a crystalline region. A cellulose fiber however is not a single crystal; it is a polycrystalline aggregate consisting of small crystal regions separated by amorphous or intercrystalline regions. The term *crystallite* is used without connoting any particular size, shape, or nature of the boundaries between crystalline regions, whereas the term *micelle* is usually used to designate a definite concept of a region having distinct boundaries.

The dimensions of the crystallite are usually assumed to be larger than the distances measured by x-ray diffraction and smaller than those visible in the light microscope. Prior to 1935, most of the chemical data which purported to measure the average size of the micelle or macromolecule were derived from methods involving disruption of the original fiber and were difficult to extrapolate back to the untreated fiber. As a result many ideas were advanced regarding the nature of the crystallite and the manner in which it is built into the fiber. Most of these ideas can be grouped generally under one or more of five theories of structure[6]; the micellar, continuous structure, secondary structure, cellulose particle, and the micellar network or fringe micellar theories. Present concepts are best expressed by a review of the micellar, continuous structure, and fringe micellar theories.

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[53] K. Hess and C. Trogus, *Ber.*, **61B**, 1982 (1928).

[54] K. Hess, H. Kiessig, and J. Gundermann, *Z. physik. Chem.*, **B49**, 64 (1941).

[55] P. H. Hermans and A. Weidinger, *J. Am. Chem. Soc.*, **68**, 2547 (1946).

(1) *Micellar Theory*

The micellar theory was first advanced by Nägeli in 1858.[56,57] He postulated that all cellulose fibers were built of submicroscopic, anisotropic

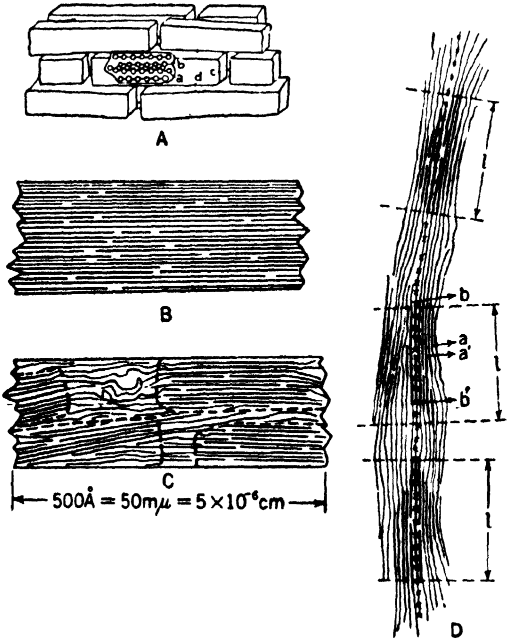

Fig. 9. Schematic representation of several possible crystallite structures (Mark[58]). (A) Micellar theory (Seifriz[59]); (B) continuous structure theory; (C) fringe micellar theory. How primary valence chains pass through more than one crystalline region (fringe micellar theory) is shown in (D). (*a*, *a'*, *b'*) Molecule ends within the crystallized region. (*b*) Molecule end outside the crystallized region. (*l*) Length of crystallized region.

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[56] C. Nägeli, *Die Stärke Körner*, F. Schulthub, Zurich, 1858.

[57] C. Nägeli and S. Schwendener, *Das Mikroskop*, 2d ed., W. Engelmann, Leipzig, 1877.

crystalline particles which he called micelles. He considered micelles to be discrete particles between which water entered to produce swelling, and although on this basis Nägeli was able to explain many cellulose properties which could not be explained by any other existing theory, his concept was not generally accepted. Later, when the existence of crystalline particles in cellulose appeared to be definitely proved, the micellar theory was adopted and expanded by Meyer and Mark[10,17] in an effort to explain the x-ray as well as the physical and chemical data. They emphasized the fact that many of the properties of cellulose are not due to cellulose molecules but to molecular aggregates or micelles made up of parallel cellulose molecules. The micelles were believed to be long, thin, submicroscopic particles arranged with their long axes roughly parallel to the fiber axis.[58,59] The fiber structure was depicted schematically by an arrangement as shown in Figure 9A in which the micelles may be compared to the bricks in a wall in that each micelle overlapped its neighbor, and was cemented to it by a mortar composed of special "intermicellar forces." Since the x-ray diagram of cellulose fibers suggested the presence of amorphous material, Herzog[60] suggested that it existed as a cementing material (*Kittstoff*) between the micelles and was responsible for the swelling of the fibers.

This concept of the existence of a separate cementing material failed to explain structures of regenerated celluloses. It was abandoned about 1930 when ultracentrifuge and viscosity methods indicated that the cellulose molecule was of the order of ten times longer than the estimated length of the micelle.

(2) *Continuous Structure Theory*

Although the x-ray data implied a discontinuous crystalline structure, there was no proof that the discontinuities had to consist of discrete crystalline particles as postulated by the micellar theory. Pierce,[61] Neale,[62] Sponsler,[63] and Astbury[64] all argued that better conformity to all types of evidence was obtained by the supposition that the molecular order only approximated crystalline perfection and was interspersed with local discontinuities as shown schematically in Figure 9B. This concept was

[58] H. Mark, *J. Phys. Chem.*, **44**, 764 (1940).

[59] W. Seifriz, *Am. Naturalist*, **63**, 423 (1929).

[60] R. O. Herzog, *Kolloid-Z.*, **39**, 98 (1926).

[61] F. T. Pierce, *Trans. Faraday Soc.*, **29**, 50 (1933).

[62] S. M. Neale, *Trans. Faraday Soc.*, **29**, 228 (1933).

[63] O. L. Sponsler, *Quart. Rev. Biol.*, **8**, 1 (1933).

[64] W. T. Astbury, *Trans. Faraday Soc.*, **29**, 193 (1933).

termed the continuous structure theory and allowed the presence of extremely long molecules as part of the continuous structure. This theory provided an adequate explanation of the physical properties of native cellulose fibers, but the micellar theory seemed more applicable for regenerated fibers. Since it seemed illogical that the structure of native and regenerated fibers would be so singularly different that widely different concepts were required to explain their physical behavior, several compromise hypotheses containing elements of both the micellar and continuous structure theories were proposed. These compromises were ultimately welded into the fringe micellar theory.

(3) *Micellar Network or Fringe Micellar Theory*

Meyer and Mark in their classical treatise on micellar structure[10] admitted the inadequacy of sharply defined crystallites as the basic structural units of fibers. This inadequacy was most strongly felt in explaining the relatively firm cohesion of fibers swollen in water in view of the observations of Katz[65,66] that water merely entered the structure between micelles and did not penetrate them. Later when Frey-Wyssling[67] and Kratky[68] postulated that a single cellulose molecule could take part in more than one crystalline region, the fringe micellar theory emerged from the work of many investigators. The development of this theory has been excellently reviewed by Frey-Wyssling[69] and Hermans[70] and needs not be discussed here.

According to this theory, the micelles are considered as statistically distributed regions of latticed order in a mass of substance consisting of approximately parallel chain molecules as illustrated schematically in Figures 9C and 9D. In the general case, the "crystalline" regions alternate with less well ordered "amorphous" regions, and within broad limits there is no connection between the length of the crystalline regions and the molecular chain length. There will be no sharply defined crystalline limits comparable to the grain boundaries in polycrystalline metals but gradual transitions along the molecules from regions of high lattice order to regions of low lattice order. The complete structure will be reticular in nature with primary valence chains anchored at various points by the high

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[65] J. R. Katz, *Ergeb. exakt. Naturw.*, **3**, 365 (1923).

[66] J. R. Katz, *Trans. Faraday Soc.*, **29**, 279 (1933).

[67] A. Frey-Wyssling, *Protoplasma*, **25**, 261 (1936).

[68] O. Kratky, *Kolloid-Z.*, **70**, 14 (1935).

[69] A. Frey-Wyssling, *Submicroscopic Morphology of Protoplasm and Its Derivatives*, Elsevier, New York, 1948, pp. 45–90.

[70] P. H. Hermans, *J. Phys. Chem.*, **45**, 827 (1941).

cohesive forces in the ordered regions holding the structure together in a coherent three-dimensional network.

For many years it was customary to define a crystalline region as a region which had the packing of one form of the cellulose single crystal as discussed previously under crystalline structure and, therefore, all other packing variations had to be considered amorphous. However, in recent years new experimental evidence has indicated that the actual case is probably a statistical distribution of packing types. The crystalline regions are not necessarily alike in different cellulose fibers nor even in different areas of the same fiber, but they will in general crystallize in some form which approximates the crystal lattice of cellulose as determined by x-ray diffraction. The crystalline regions may vary in size, but in general for a given cellulose there should be a most probable size which is dependent upon the conditions under which the original crystallization occurred. In other words, the crystalline areas in a given cellulose may vary in size, shape, and degree of perfection; thus, in order to define the fine structure of cellulose completely, it is necessary to know the complete distributions of the size, shape, and degree of perfection of the crystalline regions. Similar reasoning must be applied to the amorphous regions. At this time complete definition of cellulose fine structure is beyond the scope of our experimental methods.

The ultimate test of any cellulose fine structure theory lies in its ability to cope with the observed physical and chemical properties of cellulose, and for many years it was felt that two theories were necessary: one for native fibers and one for regenerated fibers. This necessity arose from the assumed equivalence of the crystalline regions and amorphous regions in all fibers. However when this limitation is removed by modification as discussed above, it is apparent that an infinite number of variations in crystalline–amorphous character are possible. These variations will range from a rigid crystal network in which the amorphous areas are merely lattice faults to an extremely flexible chain network in which the crystals are so small that they approach equivalence to a chemical cross-link. Present experimental evidence indicates that systems analogous to these extremes as well as many intermediate cases actually do occur and that all these variations may be considered special cases of the general case discussed. It is the authors' opinion that the fringe micellar theory, based on the presence of a coherent network structure with more or less parallel texture and modified to allow statistical order distributions, provides a sound basis for the explanation of all properties of cellulose fibers.

This theory qualitatively accounts for the deformation behavior of regenerated fibers and the changes in mechanical properties which accompany spinning and stretching.[70] If a normal chain-length distribution is assumed, the theory also allows explanations of the very high tensile strengths of native fibers and of the fact that the average chain length above a certain point no longer has a measurable influence on the tensile strength of rayons (see Chapter XI). The network structure also has a great influence on the course of most cellulose reactions, and it is generally agreed that the amorphous material is always attacked more rapidly than the crystalline material. Because of the complex nature of the cellulose structure, however, exact correlations between the various chemical and physical properties of cellulose have been possible in only a few cases. In addition, possible correlations are masked by morphological structure which so frequently is the most important factor in determining the technological uses. For example, many of the uses of wood are determined solely by the morphology or macrostructure of wood rather than by any chemical or microstructural elements. To the cellulose chemist, these macrostructures serve only to complicate the ultimate evaluation of the chemical usefulness of cellulose products. Insofar as possible, the remainder of this discussion will be limited to the submicroscopic structure which is more important for chemical utilization of cellulose.

(4) Characterization of Fringe Micellar Networks

Although, as previously pointed out, the exact definition of cellulose structures as defined by the fringe micellar theory is beyond the scope of our experimental methods, the large volume of literature devoted to methods of differentiating between different structures seems to warrant a limited discussion of the problems involved. Most of the fundamental behavior of cellulose can be best represented by a schematic statistical concept. Let us consider a structure as shown in Figure 9C and choose more or less arbitrarily a small but finite volume, V, with the only primary restriction being that it is larger than the unit cell dimensions and smaller than a volume which when packed with crystallized cellulose would behave as an infinitely large crystal. If we place this volume V at some point in the structure as an origin, it will encompass a certain number of cellulose molecules for which we can define a degree of order $\bar{O}$ by the equation:

$$\bar{O} = [OH_c]/[OH_t] \qquad (1)$$

where $[OH_c]$ is the total number of hydrogen bonds in the region and $[OH_t]$ is the total possible number of hydrogen bonds if all the molecules are perfectly crystallized. Thus $\bar{O}$ represents the degree of perfection of cellulose packing in volume V with the limits $0 < \bar{O} < 1$. Now if V is properly chosen and is translated unitwise in all directions through the fiber, it will encompass other orders $\bar{O}_1, \bar{O}_2, \bar{O}_3 \ldots \bar{O}_n$ with statistical repetition of identical orders, and the whole structure can be represented as a spectrum of order as shown in Figure 10. The quantity q_i represents the fraction of total cellulose which exists in regions having an order $\bar{O}_i$, and it is apparent that definite quantities of cellulose, $q_1, q_2, q_3 \ldots q_n$, can be associated with orders $\bar{O}_1, \bar{O}_2, \bar{O}_3 \ldots \bar{O}_n$. These quantities can be expressed summatively by the expression

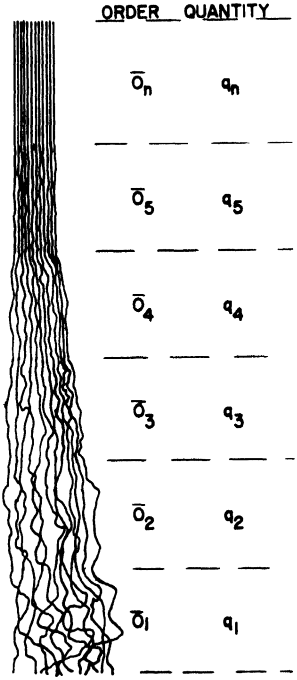

Fig. 10. Schematic mass-order distribution in cellulose. $\bar{O}$ represents order; q represents the quantity of cellulose existing at each order.

$$Q_n = \sum_{i=0}^{i=n} q_i \qquad (2)$$

in which Q_n becomes the amount of cellulose present in the sample which has an order up to and including $\bar{O}_n$. If appropriate values of Q are now plotted against corresponding values of $\bar{O}$, a summative curve as depicted i Figure 11A results. Differentiation of this curve yields a distribution curv as shown in Figure 11B which gives the relative frequency of occurrence o the volumes encompassing the various orders $\bar{O}_1$, $\bar{O}_2$, $\bar{O}_3$ . . . $\bar{O}_n$ in the structure. On this basis a cellulose fiber which consists of large crystalline regions separated by amorphous regions of fairly high order would be consistent with curve 2, and a fiber with relatively large, poorly ordered amorphous regions and small or imperfect crystalline regions with curve 1.

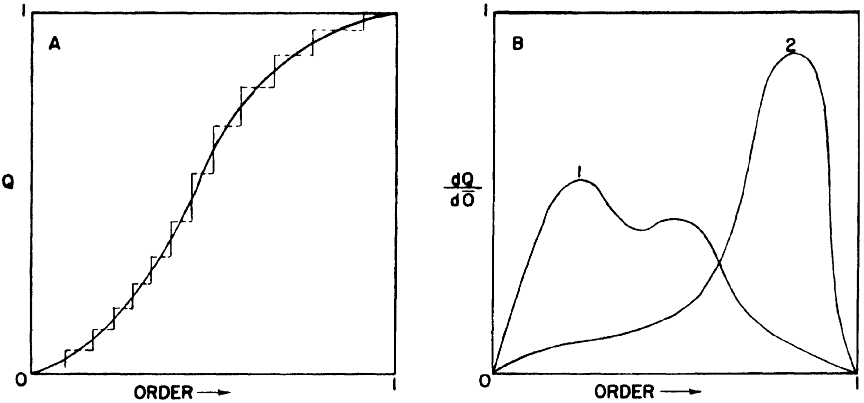

Fig. 11. (A) Summative mass-order curve for lateral order in cellulose; (B) schemati lateral-order distribution curves for cellulose: (1) low lateral order; (2) high latera order.

Although mass-order distribution concepts such as these closely depic actual order-disorder phenomena, it is interesting to note that the resolution obtained even in theory is critically dependent on the choice of th original volume element. If this volume is too large, the curves as depicted become single sharp peaks at a value of $\bar{O}$ corresponding to an average order; if too small, the curves split into two sharp peaks at zero orde and perfect order. Thus application of the principle is uncertain in man cases, but this treatment illustrates very simply the extreme difficultie encountered on actual experiment and offers a sound basis for interpretation of apparently contradictory data.

In practice no such idealized volume can be assigned experimentally t yield maximum resolution of the various degrees of order, and only fou principal characteristics of fine structure have been evaluated experimentally. These are: (1) the nature of the crystal lattice as previously discussed; (2) the size of the crystalline regions; (3) the percentage of crystalline material; (4) the orientation of the crystalline regions.

Strictly speaking none of the parameters used to measure these factors can be expressed as a single value. As early as 1933, Sisson and Clark[71] developed a method for determining average values for the crystallite orientation and the distribution of this orientation in respect to the fiber axis. With the rapid advances in high-polymer chemistry in the last few years, it has become similarly obvious that it is necessary to know not only average values of crystallite size and amount, but also the distribution of sizes and distribution of order about these averages. The advent of the electron microscope is making possible evaluation of crystallite size but as yet very few data are available on size distribution. Many methods have been proposed to evaluate the relative amounts of crystalline, nonaccessible cellulose and noncrystalline, accessible cellulose in various samples but none of them are capable of yielding order distribution evaluation as outlined previously. It seems safe to predict that such distribution evaluation will soon be possible, and it is the authors' opinion that consideration of the large masses of data available today allows reasonably intelligent empirical expression of these distributions for various widely different celluloses. For example, methods which allow the determination of the percent crystallinity or percent accessibility of the cellulose in a given sample define two quantities in accordance with the previous discussion. These quantities are:

$$Q_a = \sum_{i=0}^{i=k} q_i \qquad \text{and} \qquad Q_c = \sum_{i=k}^{i=n} q_i \tag{3}$$

where Q_c is the percentage of crystalline cellulose and Q_a the percentage of amorphous cellulose present. It is apparent that the results of any two of these methods, such as x-ray diffraction and hydrolysis will agree only when each method differentiates between "crystalline" and "amorphous" cellulose at the same order level so that the quantity summation limits are the same. This is generally not the case and qualitative order distribution trends can be observed by comparing crystallinity values obtained from different methods. Similarly, if the crystallinity or accessibility values determined by a given method such as formic acid esterification vary with experimental conditions, the variation in values obtained allows inferences to be drawn concerning order distribution. In effect, each condition alters the summative limits in equation 3 and allows summative lateral order curves to be evaluated. Since most of the published data on order parameters are expressed in terms of crystallinity, most of the following discussion will be concerned with crystallinity and only in certain well-defined cases will reference be made to complete distribution.

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[71] W. A. Sisson and G. L. Clark, *Ind. Eng. Chem., Anal. Ed.*, 5, 296 (1933).

(5) *Size and Shape of the Crystalline Regions*

A considerable volume of research has been devoted to the spatial extension and dimensions of the crystallized portions of cellulose fibers, but because of the limited applicability of most experimental methods no general conclusions were possible until data from the electron microscope became available for comparison with x-ray and chemical data.

According to x-ray diffraction theory, the breadth of the x-ray interferences of a crystalline material should depend upon the crystal size, and below a certain critical size the breadth of the interference increases in a quantitatively expressible manner with decreasing crystal size. In most cellulose x-ray diagrams this breadth is greater than that theoretically expected. In some fibers such as wood, the lines are very broad; in cotton, the lines have a medium width; in *Valonia*, they are very sharp. This implies that the average crystal size in these materials decreases in the order: *Valonia*, cotton, wood. Furthermore, in most of the fibers showing orientation of the crystalline regions, the lines arising from planes perpendicular to the fiber axis are narrower than the lines arising from planes parallel to the fiber axis. Hence the crystallized regions are long and rod-shaped. From exact calculations based on this principle, Herzog[72] and Hengstenberg and Mark[73] estimated that the micelles in ramie are approximately 50–100 A. in diameter and at least 500–600 A. long. The crystallized regions in viscose rayon were found to be about 40 A. wide and at least 300 A. long. The abnormal line breadths of cellulose diffraction patterns, however, may be related to strain in the crystal, impurities, or imperfect crystallization as well as to crystal size, and at best these figures were accepted as indicating only an order of magnitude.

A newer x-ray method for determining crystal size utilizes the evaluation of the low-angle x-ray scattering according to the theories of Guinier[74] and Kratky and coworkers.[75,76] The former was developed for dilute systems in which the distance between the scattering particles is large compared to the particle dimensions, the latter for densely packed systems. For the mean width of crystallized regions Kratky[77] found values of 70 A. in ramie and of 40 A. in regenerated cellulose filaments; these values are in good agreement with the results obtained by the line-breadth method. Using the principles of Guinier for fibers swollen in water, Heyn[78] estimated for a series of cellulose fibers that the average width ranged from 35–42 A. in ramie to 22–27 A. in jute. Again the average width for rayon fibers was found to be smaller than that for ramie fibers, and the average width for the various fibers investigated decreased in the order: ramie, Fortisan rayon, Fiber G rayon, viscose rayon, flax, hydrolyzed jute, and jute. Although the low-angle scattering method is relatively independent of most structural elements other than particle size, it is difficult experimentally, and the theory necessary for interpretation is still so uncertain that these values also represent only an order of magnitude.

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[72] R. O. Herzog, *J. Phys. Chem.*, **30**, 457 (1926).

[73] J. Hengstenberg and H. Mark, *Z. Krist.*, **69**, 271 (1928).

[74] A. Guinier, Thesis, Series A, No. 1854, University of Paris, 1939.

[75] O. Kratky, *Naturwissenschaften*, **26**, 94 (1938); **30**, 542 (1942).

[76] O. Kratky, A. Sehora, and R. Treer, *Z. Elektrochem.*, **48**, 527 (1942).

In addition to these classical x-ray methods for approximating particle sizes, large masses of data from light and electron microscopy of fibers before and after mechanical treatment of the fibers and the chemical and physical behavior of the untreated and treated products have begun to form a coherent picture in recent years. Morphologically, native cellulose fibers consist of a thin outer limiting membrane or primary wall and a thicker secondary wall. The major part of the crystalline cellulose exists in the secondary wall which under the optical microscope appears to be built up of fine fibrils aligned side by side to form layers or lamellas. These fibrils may be observed in swollen sections of the fiber after treatment with phosphoric acid[79] or dilute cuprammonium solutions.[80] They can be separated from young cellulose fibers by micromanipulators[80] and from mature fibers by the action of the papermaker's beater.[81] In all cases these apparent fibrils are just above the limit of microscopic visibility with diameters of the order of tenths of a micron. In most cases they do not lie perfectly parallel to the fiber axis but are inclined at an angle which may vary in different fibers and even in different layers of the same fiber. Fibrils in different layers within the structure may spiral in opposite direction, giving rise to a crossed fibril appearance (see Fig. 34, Section C of this chapter).

[77] O. Kratky, *Kolloid-Z.*, **120**, 24 (1951).

[78] A. N. J. Heyn, *Textile Research J.*, **19**, 163 (1949); *J. Am. Chem. Soc.*, **72**, 5768 (1950).

[79] W. A. Sisson, *Contribs. Boyce Thompson Inst.*, **9**, 239 (1938).

[80] C. W. Hock, R. C. Ramsey, and M. Harris, *J. Research Natl. Bur. Standards*, **26**, 93 (1941).

[81] A. J. Bailey and R. M. Brown, *Ind. Eng. Chem.*, **32**, 57 (1940).

The fibrillate character of native cellulose fibers has been further studied with the electron microscope which has revealed a much finer system of fibrillas below the range of microscopic visibility. A number of investigators[82-90] have utilized this method. Although their results differ widely on structural detail, there is general agreement that natural cellulose fibers are characterized by fibril structure. The diameter of the fibrils in native cellulose fibers has been variously reported from a minimum value of about 50 A.[82] to a maximum value of about 750 A.,[84] but most investigators agree on an average value around 100–150 A. Similarly, the distribution of fibril diameters has been reported to be quite uniform around 60–70 A. by Frey-Wyssling and Mühlethaler[89] and quite heterogeneous over the range from 700–800 A. down to the limit of resolution of the instrument used.[90] All investigators agree that in undegraded fibers, the fibrils are extremely long and may range up to several thousand Angstroms in length.

The wide differences in the dimensions ascribed to the fine fibrils by various investigators are probably due to a great extent to the different techniques used in preparing specimens thin enough for examination in the electron microscope as well as to possible innate differences in the samples. Therefore, direct interpretation in terms of fiber structure is difficult. There seems to be a rough relationship between the severity of the disintegration procedure and the diameter of the observed fibrils. In general, ultrasonic treatments yield finer, more uniform fibrils from undegraded fibers than does wet milling in a Waring blendor which in turn seems to yield finer fibrils with more uniform width distribution than dry or wet grinding. Chemical degradation before disintegration does not affect this general trend appreciably and again the finest fragments are obtained with ultrasonic vibration. In any event, this dependence indicates that in order to evaluate innate differences in structure, a study of both intact fiber walls and fiber walls disintegrated under carefully controlled conditions is necessary.

Two distinct hypotheses concerning the relation of these fibrillation phenomena to the original fiber structure have been presented. According to

[82] H. Ruska and M. Kretchmer, *Kolloid-Z.*, **93**, 163 (1940).

[83] E. Kuhn, *Melliand Textilber.*, **22**, 249 (1941).

[84] O. Eisenhut and E. Kuhn, *Angew. Chem.*, **55**, 198 (1942).

[85] R. B. Barnes and C. J. Burton, *Ind. Eng. Chem.*, **35**, 120 (1943).

[86] G. R. Sears and E. A. Kregel, *Paper Trade J.*, **114**, 43 (Mar. 19, 1942).

[87] E. Husemann, *J. makromol. Chem.*, **1**, 16 (1943).

[88] K. Wuhrmann, A. Heuberger, and K. Mühlethaler, *Experientia*, **2**, 105 (1946).

[89] A. Frey-Wyssling and K. Mühlethaler, *Textile Research J.*, **17**, 32 (1947).

[90] P. H. Hermans, *Textile Research J.*, **16**, 545 (1946).

Frey-Wyssling[91] these fibrillas are not preformed structural units of definite length and thickness but are fragments of a coherent submicroscopic micellar network and represent regions of good crystallization. In the original fiber these fragments are not freely movable but are connected by primary valence chains. Thus in disintegration by ultrasonic vibration, if the fiber is suspended in a swelling medium which can penetrate into the molecular network, the frictional force between vibrating liquid and the network will be greatest at the points of penetration. The mechanical strain then induced by vibration breaks first the weaker cohesive bonds between fibrils. It is also capable of breaking primary valence chains within the fibril to set free finer strands down to some limit below which further disintegration will not occur, since the finer strands assume the motion of the liquid.[92] In direct contrast to these views, Wergin[93] and Hess, Kiessig, and Gundermann[64] have put forth the view that the fiber walls consist of elementary preformed fibrils 80 to 100 A. in diameter which are assembled in bundles within some enveloping substance.

The behavior of rayons under mechanical disintegration has often been cited as evidence in favor of the doctrine of coherent network structure. Conventional viscose rayon fibers as usually made for textile purposes do not separate into long fibrils,[89] but practically all rayon fibers which have been highly stretched during manufacture to produce a high degree of molecular orientation parallel to the fiber axis will exhibit fibrillation when beaten or treated with ultrasonic vibration in the wet state.[85,89,94] In these cases preformed fibrillas in the usual sense are out of the question, and the only necessary condition for fibrillation seems to be a high degree of orientation. In this case, since any structural disintegration will occur through the planes of weakest cohesion, the tendency for longitudinal cleavage into fibrils becomes more probable with increasing orientation. This principle will also apply to native fibers, especially since the molecular orientation is usually very good in reference to the fibril axis. It would seem that the appearance of fibrils in electron micrographs of any chemically or mechanically disintegrated cellulose cannot be used as conclusive evidence that these fibrils exist as such in the original structure at the relative width and length observed. On the other hand, neither can these phenomena be used to disprove the presence of a coherent fibrillar network structure in the untreated fiber.

[91] A. Frey-Wyssling, *Kolloid-Z.*, **100**, 304 (1942).

[92] K. Mühlethaler, *Makromol. Chem.*, **2**, 143 (1948).

[93] W. Wergin, *Kolloid-Z.*, **100**, 436 (1942).

[94] F. F. Morehead, *Textile Research J.*, **20**, 549 (1950).

Very few studies of intact cell walls have been possible because of the difficulty in preparing without disintegration a sample for electron microscope study. Preston and coworkers,[95] however, have obtained electron micrographs of thin intact cell walls of *Valonia* in which the wall appears to consist of elementary fibrils of indefinite length with diameters which vary within narrow limits around 300 A. These fibrils as found in *Valonia* (Fig. 12) appear to be intrinsic features of the cell wall and are considered

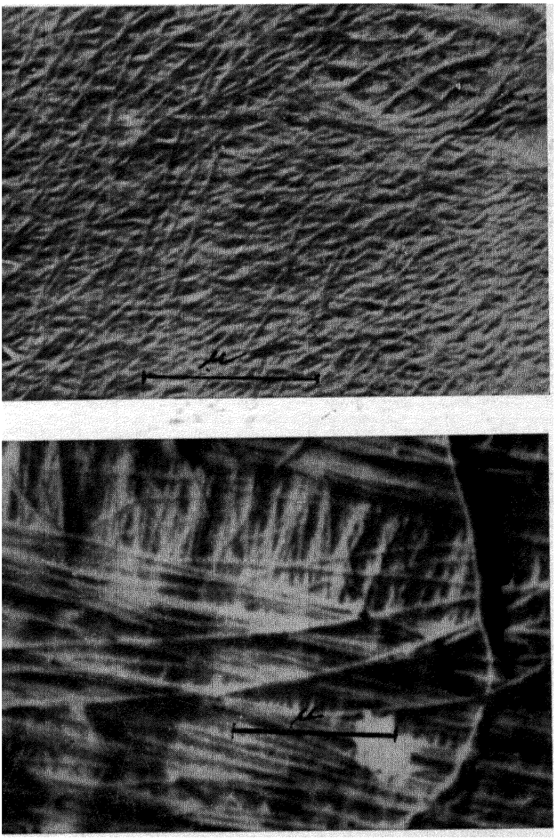

Fig. 12. (*Top*) Gold-shadowed electron micrograph of primary wall of *Avena* coleoptile, ×24,000 (Frey-Wyssling, Mühlethaler, and Wyckoff[96]). (*Bottom*) Secondary wall of *Valonia*, ×22,000 (Preston *et al.*[95]).

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[95] R. D. Preston, E. Nicolai, R. Reed, and A. Millard, *Nature*, **162**, 665 (1948).

to be fundamental building units of cellulose. Similar studies have also been reported for *Avena* coleoptiles[96] and bacterial celluloses.[97] The general explanation of the appearance of these fibrils interprets them as "crystallites" of cellulose and would imply for *Valonia* a crystallite width of 300 A. and an indefinite crystallite length. Kinsinger and Hock[98] have expressed similar views concerning fibrillation of native fibers in a Waring Blendor. They found fibrils of varying diameter and measured an average fibril width of 370 A. for ramie fibers, 150 A. for cotton, and 90 A. for wood, and pointed out that the accessibility of these fibers to hydrolytic media increased in the order of decreasing fibril diameter. This interpretation suggests that the structure within the fibril corresponds most closely to the continuous periodically distorted structure in accordance with the views of Meyer.[99] He correctly points out that in some cases there is no necessity to suppose that the crystalline fibril structure is interrupted by amorphous regions in the usual sense and compares the crystalline arrangement to that of asbestos with continuous lattice deformation. It does not seem necessary, as is so frequently done in the literature, to reject various structural theories for these reasons, and in the terminology employed here, such structures are regarded as an extreme fringe micellar case in which all structural flaws including lattice deformation are considered structural discontinuities of cohesive energy.

The suggestion that these preformed fibrils are actually crystallites of cellulose is compatible with physical behavior of native cellulose fibers but it is not completely compatible with theories of chemical behavior of cellulose. For example, the heterogeneous hydrolysis of cellulose proceeds at an extremely rapid initial rate which coincides with an equally rapid decrease in the moisture regain of the recoverable hydrocellulose. After a few minutes the rate of hydrolysis slows perceptibly while the regain either levels off or begins a slow steady increase. These effects indicate a rapid decomposition of a hygroscopic, amorphous fraction and a partial decomposition of a mesomorphous fraction. After a longer period of time the hydrolysis rate becomes constant. This constant rate period is assumed to represent hydrolysis of the crystalline component.[100] The exact relationship of this hydrolysis behavior to the original order–disorder structure of the cellulose is partially obscured by a rapid crystallization which occurs in the first few minutes of acid treatment as strain induced by crystallization forces is relieved by chain splitting.[101–103] There is, however, general agreement that only the cellulose residue remaining after hydrolytic breakdown can be considered completely crystalline and that the nature of this residue is related to the original fiber structure. In spite of the arguments presented above, there seems to be no great difficulty in reconciling the fibrillar nature of natural fibers with chemical reactivity (see Chapter IX-A).

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[96] A. Frey-Wyssling, K. Mühlethaler, and R. W. G. Wyckoff, *Experientia*, **4**, 475 (1948).

[97] A. Frey-Wyssling and K. Mühlethaler, *J. Polymer Sci.*, **1**, 172 (1946)

[98] W. G. Kinsinger and C. W. Hock, *Ind Eng. Chem.*, **40**, 1711 (1948).

[99] K. H. Meyer, *Natural and Synthetic High Polymers* (High Polymers, Vol. IV), 2d ed., New York-London, 1950, pp. 310–18.

[100] R. F. Nickerson, *Ind. Eng. Chem.*, **33**, 1022 (1941); **34**, 85, 1480 (1942).

Davidson[104] showed that the degree of polymerization (D.P.) of cellulose as measured by cuprammonium viscosity initially decreases very rapidly with time of acid hydrolysis and later approaches a limiting value which is much higher for cotton than for mercerized cotton. The rapid drop in viscosity can be accounted for by the cutting of a very small fraction of the bonds between anhydroglucose units in the amorphous regions. After a period of time when nearly all of the chains have been cut once in each amorphous region, only the exposed ends can be cut. This reaction at the exposed ends will produce only a small change in viscosity. Further investigation of these effects[105,106] has shown that the value at which the viscosity levels off is characteristic of the original sample and that the viscosities of cuprammonium solutions of residues from native structures tend to level off at much higher values than those from regenerated structures. Viscosities of mercerized structures level off at an intermediate value. This work led to the suggestion that the weight-average leveling-off D.P. determined from the leveling-off viscosity should approximate the average length of the crystalline regions in the original sample.[106] To account for crystallization during hydrolysis, Roseveare, *et al.*[107] interpret this leveling-off D.P. value as being approximately the average length of one crystalline region and one amorphous region in the original structure. Since recrystallization is never complete in the amorphous regions, it seems more reasonable to assume this length to approximate some intermediate value

[101] F. C Brenner, V Frilette, and H. Mark, *J. Am. Chem. Soc.*, **70**, 877 (1948).

[102] J. A. Howsmon, *Textile Research J.*, **19**, 152 (1949).

[103] P. H. Hermans and A. Weidinger, *J. Polymer Sci.*, **4**, 377 (1949).

[104] G. F. Davidson, *J. Textile Inst.*, **34**, T87 (1943).

[105] O. A. Battista and S Coppick, *Textile Research J.*, **17**, 419 (1947); O. A. Battista, *Ind. Eng. Chem.*, **42**, 502 (1950).

[106] R. F. Nickerson and J. A. Habrle, *Ind. Eng. Chem.*, **39**, 1507 (1947).

[107] W. E. Roseveare, R. C. Waller, and J. N. Wilson, *Textile Research J.*, **18**, 114 (1948).

TABLE 2

Cuprammonium Viscosities of Various Cellulose Materials after 30 Minutes in Boiling 2.5 N H_2SO_4 and Derived Estimates of Crystallite Length (Nickerson and Habrle[106])

Material	Cuprammonium viscosity of 0.5% soln., centipoises	Av. crystallite length calc. from viscosity as D.P.
Egyptian cotton (Malaki)	1.86	283
Linen	1.82	270
Unmercerized cotton	1.76	253
Cotton linters, acetate grade	1.75	248
Cotton linters, No. 175	1.74	244
Mercerized cotton	1.54	179
High-tenacity saponified cellulose acetate	1.40	132
High-tenacity viscose rayon	1.34	110

between these two limits. The order of magnitude of the values for different celluloses is shown by the data in Table 2. The data show that the crystallites are longest in unmodified native celluloses, that mercerization causes crystallite shortening, and that the shortest crystallites occur in viscose rayon. The crystallite length in high-tenacity saponified cellulose acetate is slightly longer than that in viscose rayon as might be expected from the method of preparation. If the extended length of the anhydroglucose unit is taken as 5.15 A. as indicated by x-ray data, and the D.P. calculated from viscosity is assumed to be correct, the lengths of these ordered regions vary from approximately 550 A. in viscose rayon to 1500 A. in cotton.

On direct examination of ultrasonically dispersed hydrolysis residues in the electron microscope, Rånby and Ribi[108] state that after profound degradation most of the cellulose has a D.P. of about 100 and that the crystalline areas appear to be of the order of 500–600 A. long and 50–100 A. wide. By similar methods Ribi[109] found crystallites from rayons to be 110–120 A. long and 70–75 A. thick and his work largely supports the general correlation between crystallite length and the leveling-off D.P. The most comprehensive work of this nature is that of Morehead[110] whose data are given in Table 3. In all cases the data refer to measurements obtained after acid hydrolysis and ultrasonic dispersion of the sample.

The close relationship between the observed particle length and the chain length calculated from cuprammonium viscosity with the sample in the "leveling-off" period of hydrolysis would seem to offer direct confirmation

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[108] B. G. Rånby and E. Ribi, *Experientia*, **6**, 12 (1950)

[109] E. Ribi, *Arkiv Kemi*, **2**, 551 (1950); *Chem. Abstracts*, **45**, 5923 (1951).

[110] F. F. Morehead, *Textile Research J.*, **20**, 549 (1950).

TABLE 3

Dimensions of Crystalline Regions in Cellulose Fibers Estimated from Cuprammonium Viscosity and Direct Electron Microscope Observation (Morehead[110])

Material	D.P	Av. chain length calc. from D P, A.	Obs crystallite length, A			Observed crystallite	
			Min.	Max.	Av	width, A	thickness, A.
Cotton	280	1440	910	2080	1440	50	64
Wood	297	1530	1200	3300	1530	37	45
Ramie........	251	1293	1120	1400	1200	35	40
Fortisan..	65	335	—	—	334	27	50
Viscose rayon	50–60	254–309	—	—	240	23	50

of the mechanism of hydrolysis as previously discussed. The exact nature of this relationship is rather startling in view of the prevalent theories of molecular-weight determination. The data also indicate that the width or thickness of the crystalline regions decreases in the order: cotton, wood, ramie, Fortisan, viscose rayon. These values agree quite well both in order of magnitude and in the relative crystal widths of various fibers determined by low-angle x-ray scattering and line-breadth methods. More recently Rånby[111] found average widths of 77, 88, 97, and 110 A. for wood, cotton, bacterial, and animal celluloses respectively.

A further check on these conclusions has been made from moisture regain and reactivity data for hydrocellulose residues. According to the hydrolysis theory previously discussed, the amorphous regions are attacked very rapidly and are either removed or recrystallized rapidly so that after some time the hydrolysis reaction is confined solely to the crystalline residue and is principally restricted to the lateral surfaces. Therefore, the moisture regain and reactivity of this residue should increase with decreasing crystal width. Since the crystalline regions are usually much longer than they are wide, the moisture regain can be assumed to be independent of the chain ends and should be a direct relative measure of the crystal width. By this method, the widths of the crystalline regions were found to decrease in the order: cotton, wood pulp, mercerized cotton, Fortisan, and viscose rayon. The average width for rayon fibers was found to be about half that of acetate-grade cotton linters.[112] Various investigators[113,114] have measured the relative rates of the hydrolysis reaction after the constant rate period has been attained and are in general agreement that the rate for different hydrocellulose residues increases in the order: cotton, wood pulps of various kinds, mercerized cotton, and viscose rayon. Since the average chain length is changing very little during this period, these values again indicate decreasing width of the crystalline residue particles in the order given.

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[111] B. G. Rånby, Inaugural Dissertation, University of Uppsala, Sweden, 1952.

[112] J. A. Howsmon, unpublished data.

[113] H. J. Philipp, M. L. Nelson, and H. M. Ziifle, *Textile Research J.*, **17**, 585 (1947).

[114] T. Timell, Dissertation, Royal Institute of Technology, Stockholm, 1950.

(6) *Crystallinity and Accessibility of Cellulose Fibers*

Since the proportions of crystalline and noncrystalline cellulose have logically been expected to influence the properties of the cellulosic material, many independent investigations have been directed toward the determination of the degree of crystallinity of cellulose. These investigations have led to widely divergent results and conclusions and much discussion relative to the comparative merits of different methods. The methods used have been principally of three types. First, there are chemical methods in which the accessible hydroxyl groups react with a reagent unable to penetrate the ordered regions of the fiber. In these cases the actual percentage of cellulose converted or the amount converted compared to some homogeneously accessible control will be a measure of the accessible cellulose present. The second class consists of methods involving kinetic studies of some chemical reaction. The course of these reactions is usually divided into an initial rapid rate followed by a slower one, and, on the assumption that the first stage involves reaction in noncrystalline regions, extrapolation of the slow-rate stage will give a value proportional to the amount of the intercrystalline material present. The third class encompasses various physical methods, all of which are based on the fact that crystalline cellulose will have different properties than noncrystalline cellulose. Thus, in general, a low degree of crystallinity is symbiotic with poor x-ray diffraction, increased extensibility, increased moisture regain, and decreased density. Proper evaluation of the contribution of the crystalline or noncrystalline portion to the total property allows estimation of crystalline–amorphous ratios.

Although some of these methods yield absolute values for the system used, none of them are absolute in defining a cellulose structure. All of these methods show a definite trend in placing the samples according to their relative crystallinity in the order: cottons as the most crystalline and high-tenacity rayons as the least crystalline. The absolute values of crystallinity determined by different methods do not agree. These different values can, for the most part, be traced to uncertainties in the methods themselves or to assumptions involved in interpretation. In view of present knowledge, although relative evaluation of different samples can be made rapidly by any one method, it does not seem advisable to make generalizations concerning structure from single-measurement methods nor to cite any one method above others without consideration of at least five factors. Briefly, these factors are: *(1) definition of terms crystallinity and accessibility for each method; (2) swelling and solubility of cellulose in the system used; (3) changes in structure, such as crystallization which may occur during the evaluation of crystallinity; (4) the effect of crystal size; and (5) the possible effects of imperfect crystallization in ordered regions.* Since at least one of these factors can be definitely shown to affect most of the crystallinity methods now in use, a brief discussion of the effects of these factors will be given before the actual results are discussed.

The schematic division of cellulose within a given fiber into crystalline and amorphous parts is significant only when the crystalline part is more or less rigorously defined, but as outlined previously such definition is not simple, and several different connotations of the word "crystallinity" have been used. For the most part these definitions have been expressed in terms of cellulose behavior under a given set of conditions and are, therefore, seriously limited by the ability of these conditions to sharply define crystalline extent. None of these experimentally determined definitions necessarily agree with the classical definition of a crystal as a region in which ideal maximal order prevails and, in fact, the best working definition probably should not agree with this classical concept. Thus, a crystalline part of any polymer has been variously defined as a region so composed that it gives rise to coherent x-ray diffraction or as a region which reacts at some slow constant rate under a given set of conditions. These definitions are not necessarily identical nor absolute, because very small regions which may exhibit maximum order will not be completely defined by x-rays whereas the definition from reaction rate may be extremely dependent on the penetration of the reactant into the cellulose structure or upon an undefined cellulose–reactant interaction of a specific nature. Fundamentally, the best criterion of what constitutes a cellulose crystal should be derived from the cellulose fiber itself, and the present tendency is to define a crystalline region thermodynamically. Thus, in respect to the cellulose fiber and its physical properties, a crystalline or ordered region can be simply defined as any unit volume containing a group of chains which will behave as a unit on application of some external force. These regions may or may not, depending upon their extent and perfection, give sharp x-ray interferences; but they will exhibit lower moisture regain, higher density, and lower chemical reactivity than other less ordered regions in the fiber.

Although chemical reactivity should be a function of the degree of crystallinity, it is actually the amorphous regions that are reactive. Hermans and Weidinger[103] are probably correct in stating that this correspondence is not exact enough for chemical methods to be an accurate measure of crystallinity. In the use of chemical methods to characterize cellulose structures the terms "accessible" and "nonaccessible" have therefore come into wide use; in direct contrast to the indefiniteness of crystallinity, the accessibility of a cellulose is an exact experimental quantity. It represents the fraction of total cellulose present which is accessible to certain reagents under certain specified conditions. As Nickerson[115] has pointed out, the determination of the accessibility of a cellulose to various reagents is far more practical than crystallinity determinations, but it is questionable that any one accessibility method is any more capable of defining cellulose structure than is any one crystallinity method. First, not only the amorphous regions but also the crystallite surfaces are accessible and the accessibility may vary with crystal size variations even at constant crystallinity. Second, if amorphous cellulose consists of a continuous spectrum of regions of varying degrees of order in which the packing of molecules varies from point to point, it follows as a corollary that the accessibility will vary with the size of the molecule and the chemical nature of the medium. Thus, the accessibility of cellulose to methanol would be expected to be greater than to butanol, and the accessibility would be lower for nonswelling than for swelling media. That this is true is illustrated by the results of Assaf, Haas, and Purves[116] who used nonaqueous thallous ethylate as the reactant and obtained the lowest accessibility values ever reported for a chemical method.

In the application of chemical methods to the definition of cellulose structures, most workers have not made adequate distinction between noncrystalline and accessible cellulose. The nonequivalence of these terms and their counterparts, crystalline and nonaccessible cellulose, is easily shown by the following relationship between crystallinity and accessibility[117]:

$$A = \sigma\alpha + (100 - \alpha) \tag{4}$$

where A is the percentage of accessible cellulose in the sample, σ is the fraction of the cellulose occurring in the surface of the crystalline regions, and α is the percentage of crystalline cellulose in the sample.

For the estimation of α from a determined accessibility, some knowledge of σ, the accessibility of the crystalline domains, is required because A will increase with decreasing crystal size and/or decreasing crystalline perfection. This equation has been used both with assumed values[117] for σ and with values calculated from experimental data[102] but, as previously discussed, the statistical nature of cellulose structure reduces its significance to that of a first approximation. The use of the equation and the crystallinity values calculated from determined accessibility illustrate fairly conclusively that the accessibility of crystals may be as large a factor in determining the reactivity of a cellulose as are differences in total crystalline content.

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[115] R. F. Nickerson, *Textile Research J.*, 21, 195 (1951).

[116] A. G. Assaf, R. H. Haas, and C. B. Purves, *J. Am. Chem. Soc.*, 66, 59, 66 (1944).

(a) **Chemical Methods for Crystallinity and Accessibility.** The basic principles for accessibility methods involving reaction of accessible hydroxyl groups have long been known. In 1929 Malm and Clarke[118] found that on boiling cotton in acetic acid with no catalyst only 6.3% acetyl could be introduced whereas viscose rayon attained an acetyl content of 22% under the same conditions. Though the authors did not comment on the significance of their results, these data are among the earliest evidence that regenerated yarns are less crystalline or more accessible than cotton. Since that time, other investigators have determined the accessibility in nonswelling media by reacting cellulose with diazomethane in ethyl ether[119]; with thallous ethylate in alcohols, ethers, or hydrocarbons[116]; or with chromium trioxide in acetic acid—acetic anhydride mixtures.[120] The accessibility values obtained from these reactions are all very low. Apparently none of these reagents penetrate the fiber to any extent unless the sample is preswollen in another medium, and the accessibility reflects principally gross structural variations. None of these methods seem capable either of characterizing the wide variations in cellulose structures normally encountered or of supplying a useful parameter for characterization of important technological properties of cellulose.

Most other chemical methods for determining accessibility utilize aqueous solutions or other swelling media and, therefore, give higher values. Of these, the hydrolysis–oxidation method introduced by Nickerson[100,106,121] was pioneering in the quantitative expression of order–disorder structures. Nickerson found that the glucose produced by cellulose degradation in 2.4 N HCl was oxidized to CO_2 in the presence of 0.6 M $FeCl_3$. The amount of cellulose hydrolyzed in a given time was set equal to the amount converted to glucose, and the actual percentage of cellulose hydrolyzed was determined indirectly by comparing the CO_2 liberated from the sample with that liberated from a known amount of glucose treated in the same way. Percentage hydrolyzed–time curves for different celluloses are all similar in shape and consist of a rapid initial rate associated with the highly reactive amorphous cellulose which gradually merges into a slower and more constant rate of hydrolysis associated with the less reactive crystalline component. The latter part of these curves, illustrated in Figure 13, allowed a rough extrapolation to zero time; the value so obtained was taken as a measure of the amount of amorphous cellulose in the sample. The Nickerson method itself was not widely used because of the laborious manipulation of data and uncertain extrapolations, but later workers simplified it

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[117] V. J. Frilette, J. Hanle, and H. Mark, *J. Am. Chem. Soc.*, **70**, 1107 (1948).

[118] C. J. Malm and H. T. Clarke, *J. Am. Chem. Soc.*, **51**, 274 (1929).

[119] R. E. Reeves and H. J. Thompson, *Contribs. Boyce Thompson Inst.*, **11**, 55 (1939).

[120] R. E. Glegg, *Textile Research J.*, **21**, 143 (1951).

[121] R. F. Nickerson and J. A. Habrle, *Ind. Eng. Chem.*, **37**, 1115 (1945); **38**, 299 (1946).

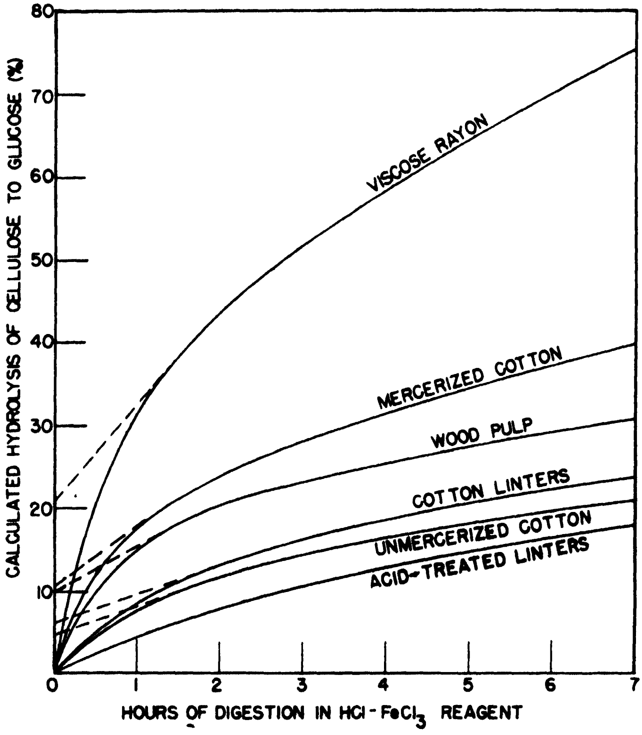

Fig. 13. Percentage of cellulose hydrolyzed versus time for various cellulosic materials in boiling 2.4 *N* hydrochloric acid–0.6 *M* ferric chloride (Nickerson[100]).

for quick routine use. Conrad and Scroggie[122] modified the analytical technique for evolved CO_2. Lovell and Goldschmid[123] measured extent of hydrolysis by following weight loss in Nickerson reagent; Philipp, Nelson, and Ziifle[113] and Nelson and Conrad[124] followed weight loss in hydrochloric acid alone. Battista[125] pointed out that relative crystallinity values could be most easily obtained by measuring weight loss after some given time, for example, 15 min., in 2.5 *N* HCl without resorting to curve extrapolations.

TABLE 4

Degree of Crystallinity of Cellulose by Acid Hydrolysis (Philipp, Nelson, and Ziifle[113])

Material	Crystalline cellulose, %
Ramie	95
Cotton	82–87
Cotton linters	88
Cotton mercerized under tension	78
Cotton mercerized without tension	68
Fortisan	83
Fiber G	81
Cordura high-tenacity rayon	62
Textile rayon	68

All of these variations of the Nickerson method yield essentially the same results. Cotton celluloses were found to contain 5 to 10% accessible cellulose; wood celluloses, mercerized cotton, and high-crystallinity rayons 10 to 15%; and viscose rayons about 25 to 35%. The principal results are given in Table 4. As is the case for all chemical methods, the amount of crystalline cellulose found varies considerably with the experimental conditions,[126] and the agreement of the above data is attributable to the general use of boiling acid. In addition, there is evidence that the amount of crystalline cellulose found by hydrolysis is dependent upon a rapid recrystallization of cellulose which accompanies chain cleavage in aqueous media. This crystallization may involve either the formation of new crystalline regions or growth of crystalline regions already present as suggested by Ingersoll[45] from x-ray data. This suggestion has been confirmed by the

[122] C. C. Conrad and A. G. Scroggie, *Ind. Eng. Chem.*, **37**, 592 (1945).

[123] E. L. Lovell and O. Goldschmid, *Ind. Eng. Chem.*, **38**, 811 (1946).

[124] M. L. Nelson and C. C. Conrad, *Textile Research J.*, **18**, 149, 155 (1948).

[125] O. A. Battista, *Ind. Eng. Chem.*, **42**, 502 (1950).

[126] A. Meller, *J. Polymer Sci.*, **4**, 619 (1949).

facts that the density [127] and x-ray crystallinity[128] increase and the moisture regain[102] decreases at a faster rate than weight is lost in the early stages of hydrolysis. X-ray diagrams of undried hydrocellulose indicate that crystallization occurs during hydrolysis rather than during drying after hydrolysis.[102]

As a general rule, recrystallization effects during hydrolysis are much more pronounced for celluloses of low crystallinity than for highly crystalline cellulose. From moisture regain data, the extent of recrystallization has been estimated at 3 to 5% for native celluloses, 10 to 15% for mercerized celluloses, and 30 to 40% for viscose rayons.[102] Roseveare[129] has shown that crystallization during hydrolysis can be inhibited by first oxidizing the accessible regions with dichromate. He found that combined oxidation–hydrolysis of a viscose rayon resulted in a 67% loss in weight whereas hydrolysis alone caused 18% loss in weight. Thus, crystallization may amount to 50% in viscose rayon and would tend to make all crystallinity values high and to compress the range of crystallinity. In spite of these effects, however, the hydrolysis method is useful as a rapid and accurate method for comparison of different celluloses.

A simple oxidation method for accessibility evaluation was advanced by Goldfinger, Siggia, and Mark[130] who reported that heterogeneous oxidation of cellulose by aqueous solutions of periodic acid or sodium periodate follows the same course as the hydrolysis reactions. Timell[114] also studied this reaction and concluded that crystallization probably occurred in use of this method according to the mechanism discussed for hydrolysis.

At least three other chemical methods which involve swelling media and which are not subject to recrystallization of the sample during the course of the reaction have been suggested. Champetier and Viallard[131] indicated that cellulose reacts quantitatively but slowly with deuterium oxide, but these investigators made no complete measurements. Frilette, Hanle, and Mark[117] showed that, with suitable rapid agitation, the reaction proceeded very rapidly during its initial stages, slowed suddenly at a certain point, and then proceeded at a very slow rate. The extent of reaction during the initial, rapid stages was taken as indicative of the amount of accessible material present and the corresponding crystallinity was calculated from equation 4. These values are given in Table 5. Since no crystallization

[127] F. C. Brenner, V. Frilette, and H. Mark, *J. Am. Chem. Soc.*, **70**, 877 (1948).

[128] P. H. Hermans and A. Weidinger, *J. Polymer Sci.*, **4**, 317 (1949).

[129] W. E. Roseveare, *Ind. Eng. Chem.*, **44**, 168 (1952).

[130] G. Goldfinger, S. Siggia, and H. Mark, *Ind. Eng. Chem.*, **35**, 1083 (1943).

[131] G. Champetier and R. Viallard, *Bull. soc. chim. France*, **5**, 1042 (1938).

occurs, the determined accessibility values are much higher than those obtained by hydrolysis. The crystallinity calculations were made on the assumption that crystal size was constant for all celluloses and that the crystal accessibility was 28%. This method is laborious, and recently the entire mechanism of the reaction has been questioned by Rowen and Plyler[132] on the basis of infrared studies which indicated that the extent of exchange was actually much lower than the value reported by Mark. However, Almin,[132a] also by infrared techniques, supports the work of Mark, and concludes that the low exchange reported by Rowen and Plyler was due to insufficient exclusion of moisture during the infrared measurements.

TABLE 5. Accessibility of Cellulose Fibers Estimated by Deuterium Oxide Exchange and Formic Acid Esterification[115,127,133]

Material	Per cent accessibility		
	by deuterium oxide exchange	by formylation[a]	by formylation[b]
Cotton	40	28	16
Various woods and wood pulps	50–55	35–47	—
Mercerized cotton	—	52	28
Fiber G	67	65	—
Cellophane	—	72	—
Textile rayon	68	—	54
High-tenacity rayon	86	77	—

[a] 98% formic acid, 15 hrs. at 55°C. [b] 90% formic acid, 12 hrs. at 30°C.

Tarkow[133] and Nickerson[115] have proposed that formic acid esterification can be used to evaluate the accessible portions of cellulose. The method involves the use of a dextrin or starch which is completely soluble in the formylation mixture as a control sample representing 100% accessibility. Then on the assumption that the esterification of starch and cellulose are identical chemical processes, the ratio of the combined formic acid, or preferably the degree of substitution (D.S.) to that of starch under identical experimental conditions can be taken directly as the fraction of cellulose accessible under those conditions. Typical accessibility values are given in Table 5 and further illustrate the general statement that determined accessibility values are specific only in terms of a given set of conditions.[112] Thus, the higher values of Tarkow can be attributed to the high formic acid concentration (98%) and high temperature used (55°C.) in comparison to the lower values (90% acid at 30°C.) used by Nickerson. Unlike the hydrolysis method, recrystallization during formylation does not occur. This was attributed to the absence of degradation in formic acid, but it is more likely due to an inhibition of any crystallization tendency by the partial substitution of the cellulose hydroxyls as shown by Baker.[47]

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[132] J. W. Rowen and E. K. Plyler, *J. Research Natl. Bur. Standards*, **44**, 313 (1950).

[132a] K. E. Almin, *Svensk Papperstidn*, **55**, 762 (1952).

[133] H. Tarkow, *Tappi*, **33**, 595 (1950).

Timell[114] studied the accessibility of cellulose by following the evolution of hydrogen from the reaction of metallic sodium with cellulose swollen in liquid ammonia. This method is of interest principally because liquid ammonia is known to form a swelling compound with cellulose[33–35] in the same manner that sodium hydroxide forms alkali cellulose. The reaction-time curves are quite similar to those shown in Figure 13 and by similar extrapolation procedures, Timell found accessibility values of 39, 43, and 58% for cotton linters, sulfite wood pulp, and viscose rayon, respectively. No crystallization occurs during the reaction and as expected the results are in closer agreement with the deuterium oxide and formic acid methods than with the hydrolysis methods. Even more interesting is the fact that the results indicate that the crystalline order in the swollen ammonia cellulose is related very closely to the order present in the original sample.

(b) **Physical Methods for Crystallinity and Accessibility.** Although x-ray diffraction procedures of cellulose fibers provided the first evidence of their crystallinity and are still the most widely used qualitative method for structure evaluation, the first quantitative methods were proposed in 1947 by Hermans[134] and Kast and Flaschner.[133] Both methods define crystalline areas as those which contribute to the maxima in the x-ray diagram and arrive at a crystalline content by comparison of the integrated x-ray intensity of the crystalline maxima and the intensity of the background scattering from the amorphous regions. The method of Hermans has been applied to a large number of fibers by Hermans and Weidinger[136–139] whose results are given in Table 6. This method is the most direct method in use. However, because of the assumptions necessary for quantitative evaluation and the fact that very small crystalline regions will not contribute to the x-ray maxima, it can be regarded only as a first approximation of the complex cellulose structure. If the uncertainties in relating crystallinity and accessibility are disregarded, the x-ray method is in best agreement with those accessibility methods which are free from possible recrystallization effects. Hermans[139] also proposed the use of the density of cellulose as a measure of crystallinity and obtained good agreement with x-ray diffraction results as shown in Table 6.

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[134] P. H. Hermans, *J. chim. phys.*, **44**, 135 (1947); *J Applied Phys*, **19**, 491 (1948).

[135] W. Kast and L. Flaschner, *Kolloid-Z.*, **111**, 6 (1948).

[136] P. H. Hermans and A. Weidinger, *J. Polymer Sci*, **4**, 135 (1949); **5**, 656 (1950); **6**, 533 (1951).

[137] P. H. Hermans, *Kolloid-Z.*, **115**, 103 (1949); **120**, 3 (1951)

[138] P H. Hermans, *Makromol. Chem.*, **6**, 25 (1951).

[139] P H. Hermans, *Contributions to the Physics of Cellulose Fibres*, Elsevier, New York, 1946, p. 70.

TABLE 6

Crystallinity of Cellulose Fibers from X-Ray Diffraction and Density Measurements (Hermans and coworkers[136–139])

Material	Per cent crystallinity from x-ray diffraction	Per cent crystallinity from density measurements
Cotton	70	60
Ramie	70	60
Valonia	65–70	—
Sulfite wood pulp	65	50
Fiber G	53	—
Fortisan	50	—
Mercerized ramie	49	39
Bacterial cellulose	40	—
Viscose rayons	40	25

The moisture sorption of cellulose consists of at least two stages: (1) selective adsorption of water molecules by hydrogen bonding to the accessible cellulose hydroxyls in amorphous regions or on crystallite surfaces. (2) physical sorption by capillary condensation or solution. These processes occur simultaneously with the first predominating at low relative humidity (see Section D of this Chapter IV). The water adsorbed by the first process, primary sorption, is strongly held by hydrogen bond forces, and the amount of this strongly sorbed water should be proportional to the accessibility of the cellulose sample to water. To estimate the quantity of the strongly sorbed water, Magne, Portas, and Wakeham[140] made use of the fact that chemically sorbed water will not freeze whereas capillary condensed or solvent water will freeze at a temperature lower than normal. The relative amounts of freezing and nonfreezing water were calculated from calorimetric data and from the amount of nonfreezing water. On the assumption that each anhydroglucose unit in the accessible regions will adsorb three molecules of water, the degree of crystallinity was calculated. The crystallinities of cotton, mercerized cotton, and Cordura rayon were found to be about 85, 77, and 52% respectively.

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[140] F. C. Magne, H. J. Portas, and H. Wakeham, *J. Am. Chem. Soc.*, **69**, 1896 (1947).

Probably the simplest and most accurate method for determining relative accessibility of cellulose to water is based on the total sorptive power. On the premise that since the nature of the sorbing substance in all fibers is the same and, therefore, that the difference in total sorptive power must be ascribed merely to differences in amount of sorbing substance, Hermans[141] postulated that the total moisture regain, especially in the range 20 to 70% relative humidity, should be a measure of the percentage of amorphous substance. These relative percentages were expressed by the sorption ratio; that is, the ratio of the moisture regain of the sample in question to that of cotton, as used by Urquhart and Williams.[142] On this basis the quantity of amorphous substance in native, mercerized, and regenerated fibers would be in the proportion 1:1.5:2. Present theories of sorption will however not allow a strict proportionality between moisture regain and the quantity of amorphous substance in the fiber. Hermans[141] first postulated this departure from linearity on the basis of x-ray diagrams of fibers. He concluded that crystalline regions of cellulose II form true hydrates whereas crystalline regions of cellulose I do not. Therefore, for a given amount of amorphous cellulose, a fiber containing crystalline cellulose II will have a higher sorptive capacity than a fiber containing crystalline cellulose I.

These original hypotheses have been generalized[117] by the postulation that the accessible hydroxyl groups contributing to sorption may be in amorphous regions, within partially disordered regions, or on the surface of crystalline regions. The contribution of the crystal surface hydroxyls cannot be ignored for, when the crystalline regions are small, a relatively large percentage of their hydroxyls are on their surfaces. Furthermore, the total percentage of the hydroxyls which lie in the crystal surface will increase with decreasing crystal size and/or decreasing crystal perfection and, therefore, the contribution of the sorption of crystal surfaces to the total sorption will increase with decreasing size or perfection of the crystals. Thus, for two celluloses with equal amounts of amorphous material, that sample with the smaller crystal size will exhibit the higher moisture sorption capacity. This view is identical with that of Hermans except that it explains the behavior of cellulose II on the basis of smaller, less perfect crystals in comparison with cellulose I samples rather than on an inherent difference in the ability of the two crystal types to form hydrates. It follows, then, that the moisture regain should be a linear single-valued function of the accessibility of cellulose to water but not a single-valued function of crystallinity in the usual sense.

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[141] P. H. Hermans, *Physics and Chemistry of Cellulose Fibres*, Elsevier, New York, 1949, pp. 180–194.

[142] A. R. Urquhart and A. M. Williams, *J. Textile Inst.*, 16, T155 (1925).

This general relation is also indicated by the close parallelism of moisture regain and the heat of wetting of cellulose fibers, but unfortunately the nature of sorption of water is not well enough defined to allow a direct determination of the percentage of accessible cellulose. The relative amounts of accessible material, however, can be expressed directly in terms of the sorption ratio or on a relative accessibility scale calibrated in terms of a particular sample. Data of this type are shown in Table 7. The accessibility scale is based on the assumption that cotton is 40% accessible to water; this value is an approximation based on deuterium oxide data and on accessibility calculated from the moisture sorption isotherm.[143] Accessibility of various cottons will vary from this figure, but the range of variability in cotton is less than for other fibers. The accessibility for all other samples is then obtained by multiplying 40 by the sorption ratio. Now it seems possible to refine the first approximation of per cent crystallinity values calculated from accessibility values as proposed by Mark and coworkers[127] by assigning different values of the accessibility of the crystalline regions for different celluloses. This has also been done in Table 7 on the assumption that the moisture regain of a sample after suitable hydrolysis is directly proportional to the accessibility of the crystalline regions. These relative crystal accessibilities are expressed as a sorption ratio on the

TABLE 7

Accessibility and Crystallinity of Cellulose Fibers as Estimated from Moisture Regain (Howsmon[112])

	Untreated		Hydrolyzed		
Material	Regain at 58% R H	Total accessibility, %	Regain at 58% R.H	Ordered region accessibility, %	Crystallinity, %[a]
Cotton	6.70	40	(5.4)	32	88
Rayaceta wood pulp	8.05	48	7.1	42	89
Mercerized cotton	10.37	62	7.5	45	69
Mercerized Rayaceta	10.45	63	8.1	48	71
Fortisan	9.60	57	8.0	48	81
Fiber G	11.00	66	—	(48)	65
Textile rayon	12.40	74	9.1	54	57
High-tenacity rayon	13.00	78	9.1	54	48

[a] Calculated by equation 4.

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[143] A. J. Hailwood and S. Horrobin, *Trans. Faraday Soc.*, **42B**, 84 (1946).

same accessibility scale used for untreated celluloses. Crystallinity values are then calculated from equation 4. The agreement between both the accessibility and crystallinity values obtained by this method and those obtained from other methods is quite good considering the fact that samples from different sources were used. None of these values can be taken as quantitative, but the trend is unmistakable that the higher general reactivity, high moisture regain, and other properties of regenerated cellulose fibers must be ascribed jointly to (1) the greater accessibility (arising from either small crystal size or imperfect crystallization) of the crystalline regions and (2) larger amounts of disordered material rather than solely to differences in crystallinity as has been most frequently assumed.

(7) *Present Status of Crystallinity–Accessibility Concepts*

It is evident from the previous topics that a large number of methods have been proposed for the determination of the relative amounts of crystalline and amorphous material in cellulose fibers. A strict comparison of the results of these methods cannot be made for the samples studied by different investigators may have varied widely in history, some of the methods refer to crystallinity and some to accessibility, and all are extremely dependent upon the definitions of the terms used in interpretation. In spite of these variations, these studies as a group lead to certain conclusions which can be regarded as generally applicable to cellulose structure and its evaluation. These general conclusions may be summarized as follows:

(1) If the absolute value of the determined accessibility or crystallinity is disregarded, all the methods rank various cellulose fibers in the same order. This applies to both chemical and physical methods in either swelling or nonswelling media. For the fibers most frequently studied, the order of decreasing crystallinity or increasing accessibility is as follows: cotton, wood pulps of various kinds, mercerized cotton, Fortisan, Fiber G, textile rayons, and high-tenacity rayons.

(2) The extremely low accessibility values obtained by methods involving nonaqueous, nonswelling media reflect principally the relative inability of these media to penetrate further than relatively gross structural faults, and, although the reaction extent and rate in these media are quite important in application to many commercial processes, they are not capable of characterizing the complex order–disorder structure beyond these gross structural features.

(3) The methods involving aqueous media allow a better differentiation

between crystalline and amorphous cellulose, and as an approximation the amount of cellulose accessible to water in cotton fibers is 30 to 40%; in wood pulps, 40 to 50%; in well ordered rayons (Fortisan, Fiber G, etc.), 55 to 65%; and in textile and high-tenacity rayon, 65 to 75%. This accessibility must be attributed not only to the presence of amorphous cellulose, but also to relatively high accessibility of small crystalline regions or regions of imperfect crystallization.

(4) The relatively high crystallinity values or low accessibility values obtained by hydrolytic methods are attributable to recrystallization of cellulose accompanying the reaction. These methods yield no direct evidence on the condition of the original sample, but they are very sensitive and are useful for comparison purposes.

(5) It is the widely accepted view that in the strictest sense none of the above methods are capable of characterizing the complex order–disorder structure beyond a first approximation and that no single measurement resulting in a simple subdivision into crystalline and amorphous cellulose components will suffice. Thus, the simple comparison of native structures and viscose rayons in terms of amorphous contents of approximately 30 and 60%, respectively, is quite misleading in that it underemphasizes the vast difference between these cellulose structures. Neither can the relatively large differences in cotton and wood pulp be explained adequately on the basis of relatively small differences in amorphous content.

It is the authors' opinion that cellulose structures can best be differentiated on the basis of the mass–order concepts discussed previously, and that although no single method is capable of yielding quantitative data of this type, fairly good qualitative representations are possible from available data such as those discussed above and other solubility, swelling, and x-ray considerations.[144] Because of the qualitative nature of the present mass–order distribution curves, it is not possible to differentiate clearly among all the variations in structure found in present commercial fibers. Most cellulose fibers, however, can be depicted roughly by one of the cases shown in Figure 14 representing the structures of cotton, wood pulp, mercerized native fibers, high-strength, low-elongation rayons, textile rayon and high-tenacity rayon. The graphic representation is the same as that discussed previously under fringe micellar networks. The amount of crystalline material, that is, the relative areas under the curves at different levels of order, is approximated from the data of chemical and physical crystallinity methods. The position of the various peaks and the shape of these peaks are approximated from reactivity, solubility, and swelling considerations coupled with evaluation of the changes in structure accompanying swelling by moisture regain, hydrolysis, viscosity, and x-ray methods. All the curves are constructed on the assumption that neither completely random packing arrangements of zero order nor perfect packing arrangements represented by an infinitely large perfect crystal will occur to any great extent. The assumed absence of infinitely large crystals can be made even though in some cases the length of the ordered regions, for example, 1500 A. in cotton, can be considered infinite because most of the chemical behavior is independent of crystal length in the normal range but greatly dependent upon crystal width for crystals less than 400–500 A. wide. Most estimates place the crystal width in cellulose fibers well below these limits.

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[144] J A Howsmon, Am. Chem. Soc. meeting, New York, September 1951.

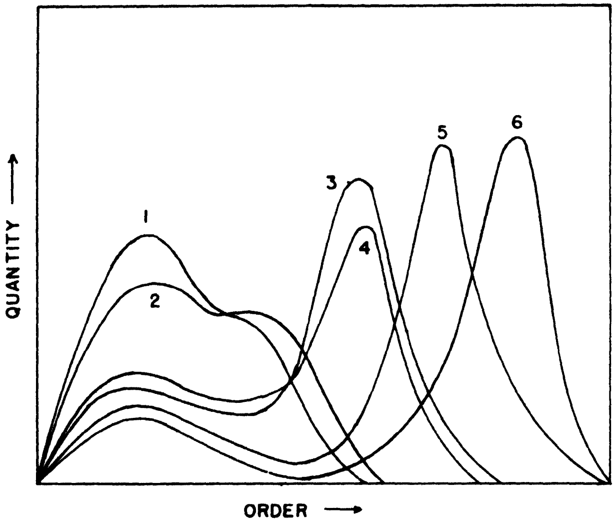

Fig. 14. Tentative lateral-order distribution curves for various cellulose fibers. Curves: (1) High-tenacity rayon; (2) textile rayon; (3) high-strength, low-elongation rayons; (4) mercerized native fibers; (5) wood pulps; (6) cotton.

Since the representation of cellulose structure in this manner is qualitative and no exact method for its determination is known, it seems advisable to review briefly the basic connection between this representation, the known properties of cellulose, and possible methods for mass–order distribution determination. This can be simply done by consideration of: (1)

swelling and solubility phenomena especially in regard to the system cellulose–sodium hydroxide–water; (2) the variation in determined cellulose accessibility with reaction conditions especially in the system cellulose–formic acid; and (3) the general application of these data to crystallinity–accessibility concepts.

(a) **Lateral-Order Distribution in and Swelling of Native Cellulose Fibers.** It is generally agreed that the solubility and swelling of high polymers are complex functions of at least two principal factors: (1) the flexibility of the chain molecule, and (2) the attractive forces between chains. Since purified celluloses from all sources can be assumed to be chemically identical except for chain length and/or chain-length distribution, the chain flexibility factor and possible variations in attractive forces between chains arising from different chain substituents can be ignored, and the differences in swelling and solubility of different celluloses in a given solvent can be attributed to differences in interchain forces arising from variations in packing perfection. A crystalline arrangement permits contact of chains along their whole length whereas in a noncrystalline state some portions of the chains will not have their attractive forces satisfied. This will result in higher solubility or swelling of a noncrystalline portion than of a crystalline portion. This behavior has been repeatedly observed. From extension of this concept to the general case, it follows that the ease of swelling will decrease with increasing chain order and with increasing size of the crystalline area. For a given solvent therefore, in which the solvent power can be progressively increased either by increasing temperature or by increasing concentration in a binary mixture, a cellulose structure characterized by a large quantity of disordered material and/or small crystallite size would be expected to swell more readily and to a greater extent in a solvent of lower solvent power than a structure characterized by a large quantity of crystalline material and/or large crystallite size. Within certain limits, the mixture sodium hydroxide–water in which the swelling of cellulose varies regularly with temperature and NaOH concentration fulfills these conditions. For a detailed description of this system and its limitations see Chapter IX-D.

In general, both the solubility (i.e., the amount of cellulose dissolved by a given solvent expressed as percentage of the original cellulose) and the swelling (i.e., increase in volume of insoluble constituents) of all celluloses pass through a maximum with increasing concentration of sodium hydroxide. Purified cotton or ramie cellulose is generally less readily swollen in aqueous NaOH than is either mercerized or regenerated cellulose. Wood pulps usually occupy an intermediate position. In general, regenerated celluloses reach a maximum in swelling at a lower alkali concentration and swell to a much greater extent than do previously mercerized celluloses which in turn swell more at a lower alkali concentration than either wood or cotton cellulose. The conclusion may be drawn that the ease and degree of swelling decrease with increasing structural organization of the cellulose, that is, as the peak in the distribution curves shown in Figure 14 shifts to a higher level of order.

It also seems possible to approximate the shape of the peaks for different celluloses from phenomena associated with the same system. Sisson and Saner[145] showed that at a given temperature there is a range of concentration of NaOH in which only partial mercerization occurs insofar as the original crystalline cellulose I structure is only partially converted to cellulose II. More recent investigations have shown that different cellulose fibers require different minimum NaOH concentrations for mercerization, and different ranges of concentration above this minimum to effect complete mercerization. This effect has been studied by x-ray[146,149] and electron diffraction,[146] moisture regain,[144,146,147,149] and intrinsic viscosity after hydrolysis (limit D.P.).[129,148,149] The results of all these studies, as illustrated in Table 8, show that treatment of native cellulose pulps with low NaOH concentrations has almost no effect on these properties. At higher concentrations the moisture regain increases, the intrinsic viscosity after hydrolysis decreases, and the x-ray diagram indicates a change in crystal form. At still higher concentrations these properties become practically independent of the concentration of the steeping solution. Comparison of data for different pulps shows that in general the modification of the structure of wood pulps occurs at a lower concentration than that required to modify cotton linters and again confirms the general position of the curves in Figure 14.

The shape of the distribution curve can then be estimated as a first approximation by plotting any one of these properties versus the NaOH concentration and determining the slope of the curve at given concentration intervals.[129] This slope is proportional to the quantity of material being modified in a given concentration interval, and when plotted against concentration, the resulting curve is quite similar to those depicted in Figure 14 as general cases. This method is generally applicable to natural cellulose fibers but is not particularly useful for mercerized or regenerated fibers because of crystallization and solubility effects. It is immediately apparent that the shape determined by this method varies with the measurement used, for in most cases the moisture regain and intrinsic viscosity change at concentrations below those required for conversion of cellulose I as measured by x-ray diffraction (Table 8). If the present hypothesis is correct in that the effects shown result from gradual dissolution of increasingly ordered material with increasing solvent power of the steeping solution, this difference is readily explained by a modification of structural elements of low order or small size below that necessary to contribute to the crystalline x-ray diagram. In this case, the most general shape for the distribution curve would be obtained from the use of the moisture regain or viscosity parameters rather than from x-ray diffraction measurements. In any event, the determination of order distribution by such procedures is not unique. Sisson and Saner[145] and Rånby[146] have shown that prehydrolysis of the sample before steeping alters the transition behavior. It does not affect the start of the transition but it favors the completion with a narrower range of NaOH concentration. Cutting cotton fibers into short lengths before steeping has a similar effect,[145] whereas the presence of lignin or other noncellulosic materials may retard the completion of the transition.[150] These effects indicate that the gradual mercerization must be attributed in part to swelling restrictions arising from fiber morphology as well as to the order of the individual structural elements. In general, the morphology contribution is not pronounced and for purified fibers the transition mechanism is as follows: at low concentrations the caustic penetrates only the low-order amorphous regions and forms alkali cellulose in the usual sense

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[145] W. A. Sisson and W. R. Saner, *J. Phys. Chem.*, **45**, 717 (1941).

[146] B. G. Rånby, *Acta Chem. Scand.*, **6**, 101 (1952); *Arkiv Kemi*, **4**, 241, 249 (1952)

[147] R. L. Mitchell, *Ind. Eng. Chem.*, **43**, 1786 (1951).

[148] L. Jörgensen, *Acta Chem. Scand.*, **3**, 780 (1949); **4**, 185 (1950).

[149] L. Jörgensen and E. Ribi, *Nature*, **166**, 148 (1950).

TABLE 8

Limit D.P., Water Regain, and X-Ray Data for Wood Pulps Swelled in Alkali Solutions of Varying Concentrations (Jörgensen and Ribi[149])

Swelling soln., wt % NaOH	Pulp 1556 (D.P. = 1700)			Pulp 1597 (D.P. = 1300)		
	Water regain, %	Limit D.P.	X-ray data	Water regain, %	Limit D.P.	X-ray data
0	6.5	240	Cellulose I	6.6	225	Cellulose I
5.5	6.6	140	Cellulose I	7.7	115	Cellulose I
6.0	8.3	95	Cellulose I and II	8.1	75	Cellulose I
7.0	8.4	80	Cellulose I and II	8.3	75	Cellulose I and II
7.5	8.7	75	Cellulose I and II	8.7	65	Cellulose I and II
8.0	8.8	55	Cellulose II	8.8	55	Cellulose II

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[150] M. K. Sen and H. J. Woods, *Biochim. et Biophys. Acta*, **3**, 510 (1949).

except for the fact that it is not crystalline in nature. The extent of this penetration increases gradually with increasing concentration until at some intermediate concentration alkali cellulose is formed in small crystalline areas or at the ends of crystallites in fringe areas which do not contribute to a great extent to the crystalline x-ray diagram. The order in these regions is lower after removal of alkali than in the original samples and probably accounts for the changes in moisture regain and viscosity after hydrolysis before any change in crystal lattice is noted. In the last stage, the crystalline regions are swollen, and the smaller or less perfect areas are transformed into crystalline alkali cellulose and then to cellulose II on alkali removal at lower concentrations than would be the larger or more perfect regions.

If these views are accepted, the difference between the reacting elements of cotton cellulose and wood cellulose as depicted in Figure 14 is fundamental and is connected with those portions usually considered to be crystalline cellulose rather than to large differences in amount of amorphous cellulose. Thus, in the general case, the ordered regions in wood cellulose are smaller or less perfect than those in cotton cellulose. Again, if the general case for wood pulp in Figure 14 is assumed to be sulfite pulp, there will be variations in pulps arising from pulp source as well as from cooking, or bleaching. These variations will cause this maximum in different pulps to shift to higher or lower levels of order,[148,149] but too few data have been published to allow characterization of these variations in terms of structure. Sulfate wood pulps have been reported to be more similar to cotton in hydrolytic behavior[129] and in transition behavior in NaOH,[144,146] and the distribution curve would be expected to show a principal peak between that for sulfite wood pulps and that for cotton cellulose. Rånby[146] has reported that bacterial cellulose has a transition interval in caustic similar to that of cotton, whereas that for animal cellulose occurs at higher caustic concentrations. Both distribution curves would be expected to approximate that given for cotton cellulose except that the principal peak for animal cellulose would be shifted to a higher order level. It is interesting to note that in each of these cases a shift in the transition interval to higher concentration is usually accompanied by an increase in the crystallite width as measured by the electron microscope. So far it is not possible to determine whether this change is solely a function of the crystallite width or a function of both width and the order present within the crystallite, but this tendency again indicates the importance of the crystalline regions in determining chemical properties of these natural cellulose fibers and pulps. Foster and Wardrop[151]

[151] D. H. Foster and A. B. Wardrop, *Australian J. Sci. Research*, **A4**, 412 (1951)

have used similar views on crystallite size distribution to explain the hydrolysis behavior of celluloses at high temperatures.

The curve for mercerized cellulose in Figure 14 is constructed for a sample in which mercerization is complete, that is, the cellulose I crystal form has been completely converted to cellulose II. The increased moisture regain, the decrease in viscosity on hydrolysis, and the increased amorphous fraction indicated by the crystallinity and accessibility methods all indicate the formation of a new network structure comprised of smaller or less perfect crystalline areas with a proportionately larger fraction of low-order material. The new crystalline areas are not only shorter as indicated by the decrease in viscosity after hydrolysis but also narrower as indicated by the x-ray work of Heyn[152] who found that the center-to-center distance

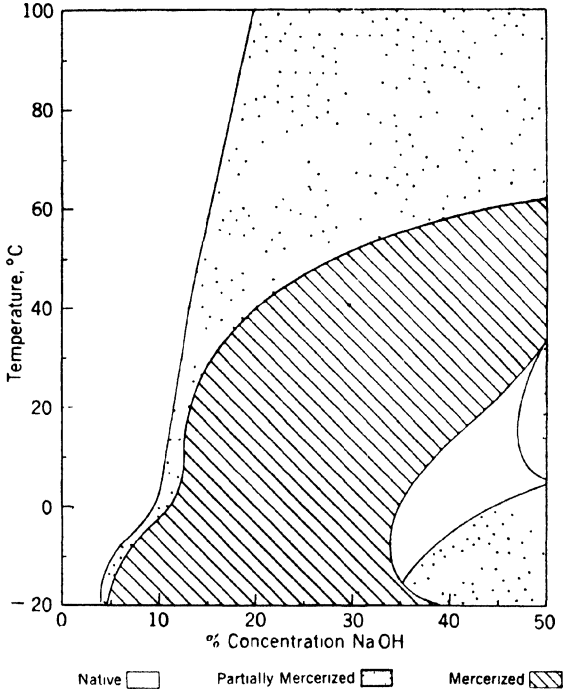

Fig. 15. Graphical representation of the effect of treating raw cotton with aqueous sodium hydroxide at various temperatures and concentrations (Sisson and Saner[145]).

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[152] A. N. J. Heyn, *Textile Research J.*, **19**, 163 (1949).

between crystalline areas decreased about 35% on mercerization. For the most part, the wide differences in properties between wood pulps and cotton celluloses are not apparent after complete mercerization because the moisture regain, viscosity after hydrolysis, and hydrolytic reactive fractions approach fairly constant levels independent of the starting material. Thus, the structure depicted for mercerized cellulose can be attributed to any completely mercerized cellulose without regard to source so long as the mercerization of the various samples is carried out under similar conditions.

Among the partially mercerized fibers, cotton fibers are of great commercial importance. Practically all commercially mercerized fibers show a mixture of the cellulose I and cellulose II structures, and variations in the extent of mercerization probably account for the variation in properties obtained by specific commercial treatments. The extent of mercerization is affected not only by the alkali concentration but also by the temperature, by the presence of tension or compression during mercerization, and by previous degradation of the fiber.

The effect of temperature and concentration on the type of x-ray diagram for raw cotton[145] after treatment with alkali is shown in Figure 15. It is apparent that complete mercerization is obtained at room temperature (20°C.) when the concentration of alkali is above 13 to 14%. The concentration required to effect complete mercerization decreases with decreasing temperature and increases with increasing temperature until at temperatures above 65°C. there is no area of complete mercerization. Furthermore, a partially mercerized cellulose may be obtained either from a cotton fiber treated with 18% NaOH at temperatures above 65°C. or from cotton treated first with cold 18% NaOH and then heated either by warming the mercerizing bath or by plunging the sample into hot water. Complete mercerization is obtained if the sample treated at a low temperature is first washed in cold water and then plunged into boiling water or if a sample treated above 65°C. is plunged into ice water. Thus the mercerization effect is determined by the final temperature provided that the temperature of the alkali-impregnated fiber is changed before the concentration of NaOH within the fiber is diluted to a concentration beyond which a reaction typical of the new temperature can take place.

When cotton fibers are oxidized or hydrolyzed by acids, the area of partial mercerization is decreased gradually as degradation proceeds.[141] This effect probably arises because continued degradative attack removes low-order regions preferentially so that the residue slowly approaches a uniform high-order distribution which will mercerize rapidly at a critical NaOH concentration. The effect of the tension on mercerization has been studied by Hess and Trogus.[153] Their experiments show that intramicellar swelling may be decreased by keeping the fibers under tension during the immersion in alkali or by stretching the fibers before and during the washing out of the NaOH. When the fibers are under tension it may be necessary to use as much as 30 to 35% NaOH to obtain the same extent of mercerization obtained with 13% NaOH on relaxed fibers. These and other experimental trials all point to the fact that any restrictive action produced either by external forces or by internal structure tends to prevent complete mercerization and, therefore, that studies of structure by mercerization procedures should be carried out under conditions which eliminate as many external factors as possible.

Although any or all of these factors may enter into commercial mercerization, the x-ray diagrams and microscopic staining procedures indicate that cottons mercerized at room temperature contain cellulose I and cellulose II structures as two separate phases homogeneously dispersed in one another. The lateral-order distribution curve for such a structure can be represented as a composite of the curves for cotton and mercerized native fibers (curves 6 and 4) in Figure 14 with peaks representing a low-order fraction, an intermediate-order crystalline cellulose II fraction, and a high-order crystalline cellulose I fraction. As the degree of mercerization increases, the high-order peak will gradually diminish. In other samples in which the partial mercerization is a result of high temperature treatment there is less definite indication of two separate crystalline phases. The inner lines of the cellulose I x-ray diagram are not clearly resolved, indicating the possibility of mixed crystallization or a relatively disordered cellulose I crystalline phase. In either case the distribution curve may still exhibit three peaks with the highest order peak being shifted to a lower order than the high-order peak of the starting material.

(b) **Lateral-Order Distribution in Regenerated Cellulose Fibers.** On treatment with aqueous alkali of varying concentration, regenerated cellulose fibers exhibit at least two distinct types of behavior. The properties of the high-tenacity, low-elongation rayons such as Fiber G and Fortisan are only slightly affected[129,144] and as a result no specific information concerning order distribution can be obtained by this method. However, treatment of tire-yarn rayons with dilute alkali results in a decrease in the hydrolytic reactive fraction,[129] a sharp increase in moisture regain at extremely low concentrations (0.5%) followed by a slow decrease with increasing concentration, and an increase in the leveling-off D.P.[154] All these facts are consistent with recrystallization of the rayon during the alkali swelling and deswelling.[156] In all cases, the first rapid changes in properties occur at lower concentrations of caustic than those required for rapid changes in wood pulp or cotton cellulose. This fact, in conjunction with the conclusions from the crystallinity methods that rayons have a larger amorphous fraction and a more highly reactive crystalline fraction than native celluloses, suggests the shift in the principal features of the order distribution curves for rayons to the lower energy levels as shown in Figure 14, but again the indications are only qualitative.

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[153] K. Hess and C. Trogus, *Z. physik. Chem.*, **B4**, 321 (1929); **B11**, 381 (1931).

[154] O. A. Battista, private communication.

The formic acid accessibility method of Nickerson[115] can also be used to characterize the shape of these curves especially for the various rayons. Work in the authors' laboratory involving a modification of Nickerson's method indicates that in general the determined accessibility of a cellulose to formic acid increases with increasing temperature in the range of 7° to 55°C. and with increasing formic acid concentration, and that the magnitude and rate of change of this accessibility with a change in a given variable such as temperature vary with the type of cellulose. This tendency is evident from the data in Table 9 which show the accessibility of various celluloses to 90% formic acid at various temperatures. Thus, cotton and wood pulps have low accessibility with relatively small changes with temperature; Fortisan rayon has an intermediate accessibility which increases rapidly with increasing temperature; and high-tenacity tire-yarn rayon has a high initial accessibility which rapidly increases with increasing temperature. These data confirm the relative shapes of the curves in Figure 14 and point out clearly that practically all the material present in a tire-yarn rayon is accessible under conditions for which cotton is only 20%

TABLE 9

Variation of Accessibility of Cellulose to 90% Formic Acid with Temperature (Howsmon[112])

Sample	Per cent accessible cellulose at 7°C.	30°C.	55°C.	Per cent nonaccessible cellulose at 55°C.
Cotton linters (Hercules)	15	16	22	78
Rayaceta wood pulp	19	22	27	73
Mercerized cotton (Hercules)	32	43	54	46
Fortisan	21	32	48	52
High-tenacity rayon	51	77	94	6

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[156] P. H. Hermans, D. Vermaas, and A. Weidinger, *Nature*, **165**, 238 (1950).

accessible. Curve 3 given in Figure 14 for Fortisan should be quite characteristic of other highly crystalline fibers such as Fiber G, and curve 1 given in Figure 14 for high-tenacity rayon should be characteristic for all commercial viscose tire yarns. Practically all viscose textile yarns are almost identical structurally and are characterized by curve 2 in Figure 14.

For most viscose rayons, however, the case is not quite so simple. The presence of a "skin effect" in viscose rayon has been the subject of considerable inquiry since it was first demonstrated by Preston,[156] Ohara,[157] and Schramek and Helm.[158] It has been shown that most viscose rayons have a cortical layer or "skin" which on dyeing differs markedly in behavior from the center or "core" layer of the filament. Usually the core absorbs dyes more quickly than the skin but once dyed, the skin retains the dye longer on subsequent washing.[158,159] Preston and coworkers[156,160,161] explain this differential dye absorption principally on the basis of a higher degree of orientation in the skin. According to Morehead and Sisson,[162] however, the orientation dependence of skin behavior is not in harmony with the fact that rate of spinning and stretch during spinning have little effect on skin formation and that viscose extruded freely under no tension into a bath will possess skin when the skin-forming bath and viscose conditions are used. These workers conclude that the staining differential between skin and core is primarily a matter of crystallization rather than orientation and that skin is usually formed under conditions which tend to favor good orientation and poor crystallization.

The exact structural difference between skin and core is difficult to demonstrate experimentally, but most data support the crystallization theory of Morehead and Sisson. Although Hermans[159] found no evidence of lower crystallinity from x-ray diffraction crystallinity determinations, the lateral-order measurements of Ingersoll[45] from x-ray diffraction indicate poorer crystalline order in thick-skin yarns. In addition, the moisture regain[162,163] and reactivity[164] increase with increasing skin thickness whereas the crystallinity by hydrolysis[164] and density[159] decrease. Both x-ray diffraction and

[156] J. M. Preston, *J. Soc. Chem. Ind.*, **50**, T199 (1931).

[157] K. Ohara, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **25**, 152 (1934).

[158] W. Schramek and J. Helm, *Kolloid-Z.*, **85**, 291 (1938); *Cellulosechemie*, **18**, 1 (1940).

[159] P. H. Hermans, *Textile Research J.*, **18**, 9 (1948).

[160] J. M. Preston and R. V. Bhat, *J. Textile Inst.*, **39**, T211 (1948); J. M. Preston and K I. Narasimhan, *J. Textile Inst.*, **40**, T327 (1949).

[161] J. M Preston and G. D. Joshi, *Kolloid-Z.*, **122**, 6 (1951).

[162] F. F. Morehead and W. A. Sisson, *Textile Research J.*, **15**, 443 (1945).

[163] J. A. Howsmon, unpublished results.

[164] O. A. Battista, *Ind. Eng. Chem.*, **42**, 502 (1950).

birefringence measurements indicate that the uniaxial orientation is higher in the skin portion than in the core portion.

All these facts are consistent with the original premises of Morehead and Sisson. The following tentative hypothesis for skin and core structures therefore seems most plausible at this time. The skin is formed under conditions which favor the formation of a relatively large number of crystal nuclei but tend to inhibit perfect crystallization. The network structure set up under these conditions is comprised of small crystalline and small amorphous areas. Such a network is strong and tough because each molecule will pass through a greater number of crystallites as the crystallite size decreases, and is flexible because of a high structural plasticity which increases with decreasing crystallite size.[162,165] Furthermore, swelling and dye penetration are limited by the shortness of the connecting chain segments between crystallized areas even though the total amount of low-order material is high. The core, on the other hand, is formed under conditions which favor the formation of fewer crystal nuclei and their subsequent growth to larger crystallized areas which in turn are separated by large amorphous areas. This type of network will allow greater swelling and dye penetration even though the average order may be higher than in the skin, but the network will be less tough and flexible because of the relatively low structural plasticity arising from the large crystalline regions.

The net result of the skin–core structure in viscose rayons can be expressed quantitatively in terms of lateral-order distribution, and it is obvious that the curves depicted in Figure 14 represent an average distribution for skin and core structures. Thus curve 1 in Figure 14 for high-tenacity rayons represents a summation of a curve for the skin containing extremely small crystals of low order and a curve for the core which can be represented by a curve similar to that shown in Figure 14 for textile rayon shifted slightly to a higher order level. The displacement of the high-tenacity rayon to the left of the textile rayon is in direct relation to the thicker skin found in all high-tenacity rayons. The distribution curves for other cellulose fibers such as cuprammonium rayon, Fiber G, and Fortisan are not subject to these uncertainties for none of these fibers exhibit pronounced skin and core effects.

(8) *Relationship of Crystallinity to Physical Properties*

Although few quantitative studies have been made of the exact variation of cellulose properties with crystallinity, the reported effects of increasing

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[165] S. E. Sheppard and P. T. Newsome, *J Soc. Chem. Ind.*, 56, 256T (1937).

crystallinity on some fiber properties are listed in Table 10. These reported effects, even though only qualitative, adequately confirm the long-suspected influence of ordered regions in fibers as proposed by Mark[58] and Hermans.[166]

TABLE 10

Effect of Increasing Crystallinity on Properties of Cellulose Fibers

Increases	Decreases
Tensile strength	Elongation
Young's modulus	Moisture sorption
Hardness	Swelling
Dimensional stability	Dye sorption
Density	Toughness
	Chemical reactivity
	Flexibility

They concluded that the physical properties such as tenacity, elongation, and elasticity are functionally related to the amount and kind of crystalline material, whereas the reactivity and swelling are closely associated with the amorphous areas. Baker, Fuller, and Pape[167] have shown that toughness and extensibility in cellulose esters are favored by local molecular disorder and point out that these phenomena are presumably general for all linear polymers. The general nature of the relationships set forth in Table 10 is illustrated by the data[168] in Table 11 showing the elongation of cotton fibers at constant orientation but diminishing crystallinity. These factors are discussed in greater detail in Chapter XI.

TABLE 11

Variation in Crystallinity and Elongation (at Constant Orientation) with Amine Treatment of Cotton Yarns (Ward[168])

Treatment	Degree of crystallinity, %	Elongation, %
Bleached and kiered 20/1 yarn (untreated control)	91.0	5.4
Treated with ethylamine, followed by water boil, 1/2 hr.	74.2	13.0
Treated with ethylamine, followed by water boil, 2 hrs.	58.7	12.3
Treated with ethylamine, followed by hexylamine	37.2	16.0

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[166] P. H. Hermans, *J. Phys. Chem.*, **45**, 827 (1941).

[167] W. O. Baker, C. S. Fuller, and N. R. Pape, *J. Am. Chem. Soc.*, **64**, 776 (1942).

[168] K. Ward, *Textile Research J.*, **20**, 363 (1950).

These results do not mean that the elongation of a cellulose fiber will always decrease nor that the tensile strength will always increase with increasing crystallinity. In considering the effects of crystallinity on properties, it is difficult to isolate crystallinity from orientation, the latter usually having a much more pronounced effect on physical properties. Even at constant crystallinity and orientation, other factors—either extraneous mechanical factors or structural details, such as imperfections, crystal size, or general morphology, not differentiated by the particular crystallinity method used—may operate to change the properties. For example, even though the relative properties of viscose rayon, Fiber G, Fortisan, and native fibers uphold the general premise that tensile strength increases and elongation decreases with increasing crystallinity, within a given group of viscose rayon fibers both wet tenacity and wet elongation are found to

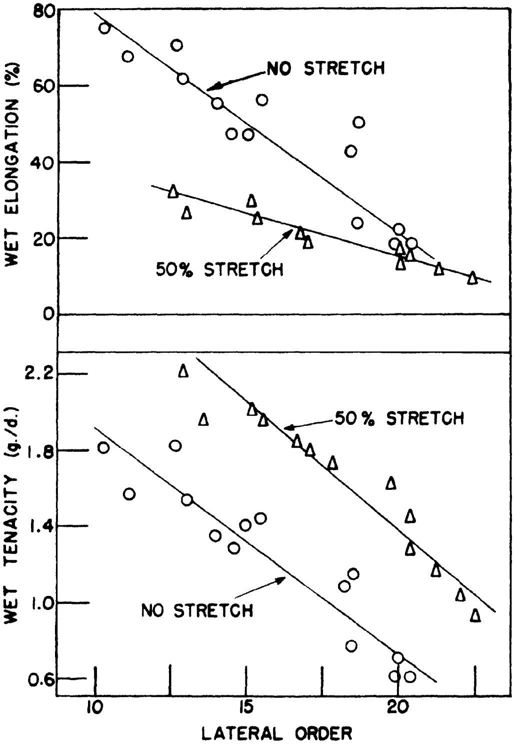

Fig. 16. Wet tenacity and wet elongation as functions of lateral order for stretched and unstretched experimental viscose rayons (Howsmon[163]).

decrease significantly with increasing lateral order as measured by moisture regain (Fig. 16). Ingersoll[15] first noted these correlations with the lateral order as measured by x-ray diffraction, and pointed out that in each correlation the specific relation sought may be obscured by other variables which have not been held constant. For example, both wet tenacity and orientation are also related to wet elongation, and the observed relation between wet elongation and lateral order may be affected by accompanying changes in wet tenacity and orientation. By statistical methods, Ingersoll found that wet elongation was still significantly related to lateral order at constant orientation and wet tenacity, but the relation between wet tenacity and lateral order was no longer significant at constant orientation and wet elongation. He concluded that the apparent relationship shown was merely a result of simultaneous variations in wet elongation and the dependence of wet tenacity upon wet elongation which are still significantly related even at constant lateral order and orientation. These correlations suggest that the stress–strain curves of these rayons are quite similar and that the yarns fail at different elongations. The exact role of fine structure in determining these property variations is not yet clear, but the general applicability and limitations of the correlations with crystallinity noted here should become more clearly defined as the methods for evaluating structure are refined and data become available on the structure and properties of yarns prepared under a wider variety of conditions.

(d) ORIENTATION

In the widest sense, the term orientation should refer to the alignment of individual molecules relative to one another and to the surfaces of a sample, but in this sense the term does not lend itself to quantitative expression because of the coexistence of the ordered and disordered phases of fiber structure. For this reason, the term orientation is most often used only for reference to the crystallized regions for which orientation measurements can be made. In the present discussion, therefore, orientation will refer principally to arrangement or alignment of cellulose crystalline regions in respect to the fiber axis or to the fiber surface. It will have no reference to the orientation of individual molecules within a crystalline region except in the sense that crystallite orientation determines the orientation of all of its component molecules. Since the orientation of individual molecules within a noncrystalline region may vary from point to point and from fiber to fiber, reference will be made to the orientation within amorphous or low-order regions. In this case the term orientation will refer exclusively to the alignment of individual molecules. It is thus theoretically possible to have an amorphous fiber with parallel molecular orientation or a crystalline fiber with random crystallite orientation, and within limits the orientation can be changed without appreciably affecting the crystallinity, or vice versa. It may also be possible to have a fiber with good crystallite orientation and good molecular orientation within disordered regions for though high molecular orientation corresponds to greater one-dimensional crystallinity, such regions will not have crystalline properties unless reasonable three-dimensional order is attained.

(1) *Types of Orientation*

The general term orientation, as used in the literature, usually refers only to the alignment of the long or molecular axes of the crystallites in respect to the fiber axis, but it is possible to have other types of orientation which may be identified from the x-ray diagrams and classified as follows:[169]

(1) Random orientation. The crystallites lie in all possible directions and the same x-ray diagram is obtained with the sample at any angle to the x-ray beam. (See Fig. 17a; all diagrams in Fig. 17 are schematic and refer to the cellulose I crystal form; cf. Fig. 7.)

(2) Uniplanar orientation. For this type of orientation, the only limitation imposed is that the *b* or long axes (chain direction) of the crystallites lie parallel to a plane. The crystallites lie at random in the plane and have all possible rotations around the *b* axis. With the *a* axis parallel to the x-ray beam, the diagram is random with all lines present; with the *b* or *c* axis parallel, a fiber pattern is obtained with all lines present as arcs on the equator (see Fig. 17b).

(3) Selective uniplanar orientation. This type of orientation is similar to uniplanar orientation in that the *b* axes are parallel to and arranged at random in a plane; the added restriction is that the 101 planes of the crystallite have a selective orientation parallel to a plane which is usually the large surface of the specimen (see Fig. 17c). With the *a* axis parallel to the x-ray beam, a random diagram is obtained with the 101 line missing and the $10\bar{1}$ present; with the *b* or *c* axis parallel, the 101 line is present as a dense arc on the equator, whereas the $10\bar{1}$ line is present only as a faint arc on the meridian.

(4) Uniaxial orientation. For this type of orientation the only limitation imposed is that the *b* axes of the crystallites have a preferred orientation parallel to the fiber axis. With the *a* or *c* axis parallel to the x-ray beam, the 101, $10\bar{1}$, and 002 lines all exist as intensity maxima at the equator and

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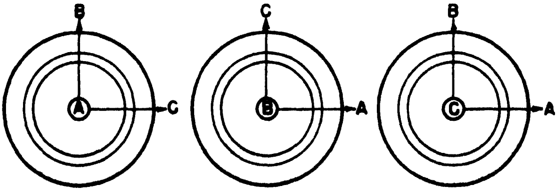
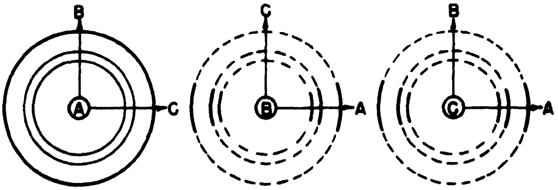
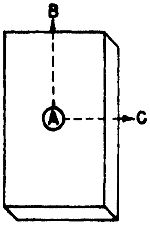
[169] W. A. Sisson, *J. Phys. Chem.*, **40**, 343 (1936).



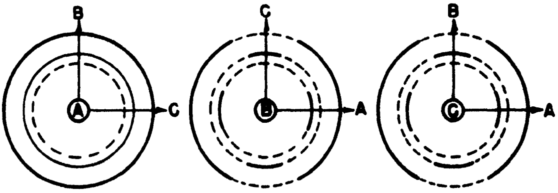
(a) RANDOM ORIENTATION



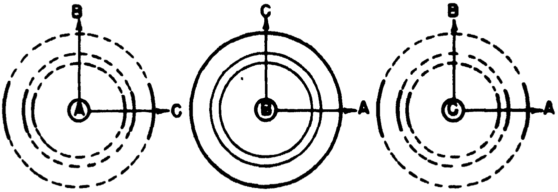
(b) UNIPLANAR ORIENTATION



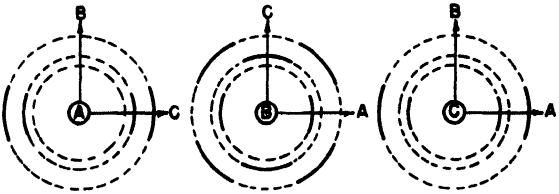
SAMPLE



(c) SELECTIVE UNIPLANAR ORIENTATION



(d) UNIAXIAL ORIENTATION



(e) BIAXIAL ORIENTATION

Fig. 17. Schematic x-ray diagrams of cellulose fibers illustrating the five general types of orientation.

axis[45,179]; and (4) the orientation factor, f_r, which is related to an average angle of orientation determined by graphical integration of the intensity distribution curve.[180]

(a) **Orientation in Native Cellulose Fibers.** The exact measurement of orientation in many natural cellulose fibers is complicated by the morphology of these fibers in that the fibers consist of concentric cylindrical lamellas which in turn are composed of fibrils. These fibrils spiral around the long axis of the fiber, and the exact expression of orientation must account not only for the orientation of crystallites within the fibril but also for the orientation of the fibrils in respect to the fiber axis. In a natural fiber possessing spiral structure, the x-ray diagram does not represent the true orientation. With the x-ray beam perpendicular to the fiber axis, the x-ray diagram represents the three-dimensional orientation of the crystallites projected on a plane. The density distribution around the x-ray diffraction ring is always shifted toward the equator because of the cylindrical form of the fiber, and the fibrils in that portion of the cell wall parallel to the x-ray beam diffract on the equator rather than at an angle corresponding to the spiral angle. These same factors also cause anomalous results when the orientation is measured by the refractive index method.[181]

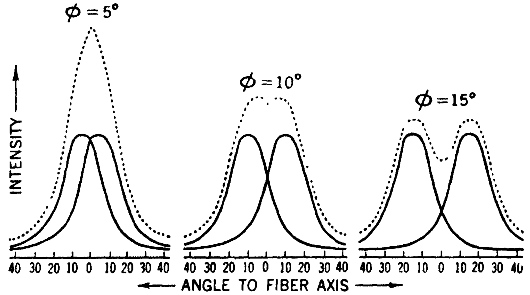


Fig. 18. Theoretical x-ray intensity distribution curves for cellulose fibers having various angles of spiral orientation (Sisson[18b])

The type of x-ray intensity distribution curves to be expected from well-oriented spiral structures is shown in Figure 18. These curves show that: (1) the total distribution (upper dotted line) is a function of both the spiral angle, ϕ, and the distribution about this angle; (2) the x-ray pattern may not indicate a spiral structure although one is present; (3) in order to obtain an x-ray pattern showing the four intensity maxima of a spiral structure, the spiral angle must be large and the deviation from the spiral angle must be small; and (4) the maxima of the x-ray intensity curve may not correspond to the actual spiral angle. Actual density curves and the angle of spiral are shown in Figure 19 for four natural fibers. It can be seen, for example, that cotton and compression wood have about the same spiral angle but the deviation from this angle is greater in cotton.

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[180] J. de Booys and P. H. Hermans, *Kolloid-Z.*, **97**, 229 (1941).

[181] R. D Preston, *Trans. Faraday Soc.*, **29**, 73 (1933).

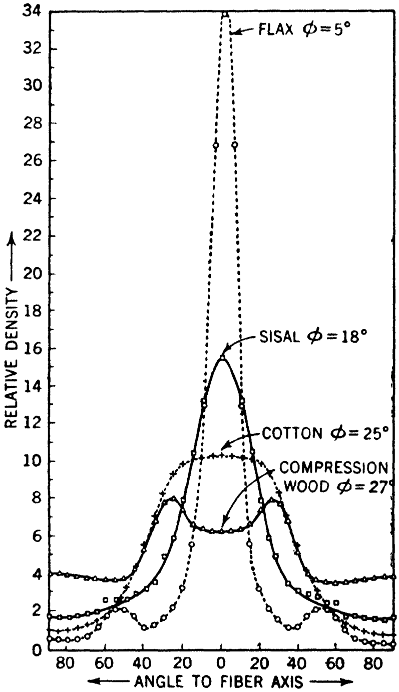

Fig. 19. Measured density distribution curves around the 002 diffraction ring for several natural fibers (Sisson[188]).

The exact nature of these lamellar fibril structures is best illustrated by studies of the marine alga, *Valonia ventricosa.* Sponsler[182] first pointed out that these large cells could be split longitudinally and by taking x-ray diagrams of flat pieces of *Valonia* cell wall was able to show that the (101) planes were selectively oriented parallel to the surface of the wall. Later Astbury, Marwick, and Bernal[183] showed that two principal sets of crystallites crossed one another in the cell wall at an angle of approximately 80°. Subsequent microscopic studies[184,185] have shown that *Valonia* is built up of two sets of fibrils crossing at about an angle of 80°, as shown in Figure

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[182] O. L. Sponsler, *Protoplasma,* **12,** 241 (1931).

[183] W. T. Astbury, T. C. Marwick, and J. D. Bernal, *Proc. Roy. Soc.* (*London*), **B109,** 443 (1932).

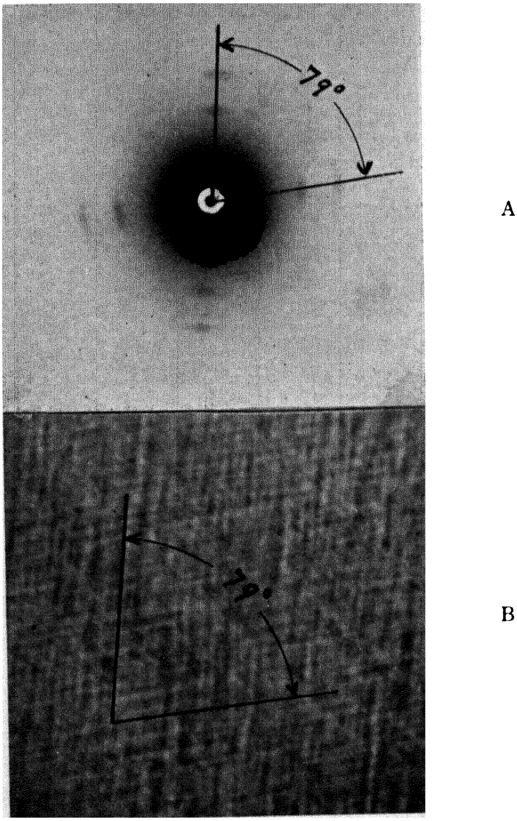

Fig. 20. X-ray diagram (A) and photomicrograph (B) of *Valonia* taken perpendicular to the membrane surface showing the direction of fibril and crystallite orientation (Sisson[184]).

20B. X-ray diagrams of the same sample show the usual equatorial diffraction lines concentrated into four arcs with the sets approximately 80° to one another, as shown in Figure 20A. The dispersion from perfect crystallite orientation can be completely accounted for on the basis of

[184] W. A. Sisson, *Contribs. Boyce Thompson Inst.*, **12,** 171 (1941).

[185] R. D. Preston and W. T. Astbury, *Proc. Roy. Soc.* (*London*), **B122,** 76 (1937).

observed deviation in fibril orientation. Thus by comparison of x-ray diagrams and photomicrographs of the same sample it has been shown indirectly that the long axes of the cellulose crystallites are arranged parallel to the axis of the fibril and that the fibril possesses biaxial orientation. It has been possible in most natural fibers to account for the observed orientation in x-ray diagrams on the basis of fibril orientation observed in the microscope. For example, the high orientation in flax fibers (Fig. 19) and the rather wide deviation from parallel orientation in cotton fibers (Fig. 21) can be directly related to the fibril orientation observed in the cell wall.

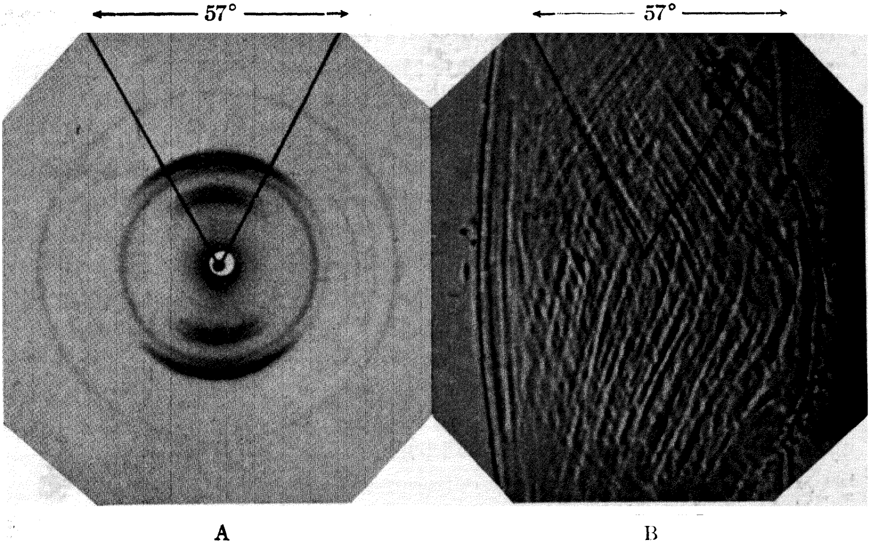

Fig. 21. Comparison of x-ray and fibril orientation (Sisson[79]). (A) X-ray diagram of mature cotton; (B) photomicrograph of cotton fiber swollen in phosphoric acid to show fibril structure.

These conclusions obtained indirectly seemed at first to be disproved by electron micrographs in which fibrils of varying diameter were obtained by mechanical and chemical disintegration of cellulose fibers.[82–90] However, later workers[95–97] showed the innate fibrillar structure of intact cell walls of *Valonia*,[95] *Avena* coleoptiles,[96] and bacterial cellulose,[97] and the basic relationships between fibril and x-ray orientation need not be changed except in respect to the smaller fibril size revealed in electron micrographs. Therefore, the remainder of this discussion will concern principally the spiral orientation and deviations from the spiral angle in natural cellulose fibers.

Natural cellulose fibers, regardless of their appearance, exhibit x-ray diffraction patterns characteristic of orientations ranging from nearly perfect parallel fiber structure to almost completely random arrangements. Relatively few quantitative studies of orientation for a large number of fibers are available and the observed orientations have been found to vary from fiber to fiber, along the length of the fiber, and among different species and varieties of a given fiber type. Thus, it is almost impossible to state definitely the degree of orientation in various natural fibers. However, a rough classification of natural fibers can be made and illustrated by the orientation distribution curves in Figure 19.

The bast or soft fibers as illustrated by the curve for flax in Figure 19 are generally characterized by orientation almost parallel to the fiber axis. The spiral angle is of the order of 5° and deviation of fibril orientation from this angle is small. Hemp fibers usually have slightly better parallel orientation than flax or ramie,[186] and ramie has slightly better orientation than jute.[187] Within the leaf or hard fibers wider variations in orientation from species to species are found than in the bast fibers; also as a rule even though deviations from the spiral angle may be small, the spiral angle is greater than in the bast fibers. These fibers are characterized by the curve for sisal in Figure 19. Berkley[186] found that the spiral angle increased in the order abacá, sisal, sansevieria, and henequen. The probable range of spiral angles lies from 10–15° in abacá to the order of 25° in certain agave fibers.[78] The distribution curves will then vary in shape from that shown for sisal to the curve shown for compression wood in Figure 19. The list of minor vegetable fibers is long, and few orientation data are available. A wide range of orientation characteristics have been observed varying from a fairly parallel arrangement in kapok to arrangements with very large spiral angles in yucca, bamboo, Spanish moss, and coir fiber.[78,182,188] The spiral angle of 45° in coir fiber is the largest reported.

Cotton fibers, although indicated by a single curve in Figure 19, show the greatest variations in spiral angle of any fiber studied.[176,177,188] The deviation from the spiral angle is usually large so that the distribution curve shows only a single peak, and exact evaluation of the spiral angle has not been made in all cases. The 40% x-ray angle[176,188] may vary from 18° to 52°. These angles, which increase with decreasing orientation, are only indices of the true spiral but may be taken as indicative of the large differences found. The x-ray angles have been found to be reliable indices of genetic characteristics and environmental conditions of cotton fibers and are widely used in cotton breeding and research.[177]

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[186] E. E. Berkley, *Textile Research J.*, **19**, 363 (1949).

[187] M. K. Sen and H. J. Woods, *Proc. Leeds Phil. Lit. Soc*., *Sci. Sect.*, **5**, Pt. 2, 155 (1949).

Wood fibers also exhibit wide variations in orientation but again relatively few quantitative studies are available.[188–196] The variations range from nearly perfect parallel orientations to parallel orientation at a definite spiral angle to the fiber axis (Fig. 19) or spiral orientations with large deviations from the spiral angle as in cotton. The observed orientation may also vary in the radial and tangential walls of the wood cells.[193,194] In general, there is great variation in orientation depending upon the species of wood, the season of growth, and the position of growth.[196] Clark[193] has reported that the preferred orientation in various woods decreases in the order: Douglas fir, spruce, cedar, hemlock, and loblolly pine. Such orders may be disturbed however by growth season and position of the sample studied. Thus, summerwood is usually more perfectly oriented than springwood.[191,193] Compression wood usually exhibits a large spiral angle with small deviations from this angle[196] (Fig. 19). The cellulose crystallites are usually in a random orientation for several inches from the growing tip, but almost perfect parallel orientation is frequently found on the top of the branch between this point and the parent branch or trunk. Many other variations including three distinct spirals in sequoia wood[194] have been observed but many of them cannot be clearly interpreted at this time.

In native fibers the questions arise as to when during growth the orientation occurs and whether or not the crystallites have a selective orientation in respect to the cell wall similar to that observed for *Valonia*. Most studies of these effects have been carried out on cotton and wood fibers. In the first x-ray examination of young cotton fibers,[197] evidence of orientation was not found in samples younger than 35 days. Subsequent work[79] showed that, in general, cotton fibers younger than about 25 days give x-ray diagrams of randomly oriented cellulose; between 25 and 35 days a preferred orientation develops which does not change appreciably with

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[188] W. A. Sisson, *Ind. Eng. Chem*., **27,** 51 (1935).

[189] R. D. Preston, *Chronica Botan.*, **7,** 414 (1943).

[190] I. W. Bailey and E. E. Berkley, *Am. J. Botany,* **29,** 231 (1942).

[191] W. L. Caldwell and K. Lark-Horowitz, *Nature,* **134,** 23 (1934); *Phys. Rev*., **51,** 998 (1937)

[192] G. L. Clark and J. A. Howsmon, *Ind. Eng. Chem.*, **38,** 1257 (1946).

[193] G. L. Clark, *Tappi,* **33,** 108 (1950); *Ind. Eng. Chem.*, **22,** 474 (1930).

[194] E. E. Berkley and O. C. Woodyard, *Textile Research J.*, **18,** 519 (1948).

[195] G. J. Ritter and C. W. Stillwell, *Paper Trade J.*, **98,** 37 (May 31, 1934).

[196] C. W. Stillwell, *Crystal Chemistry,* McGraw-Hill, New York, 1938, pp. 377–381.

[197] G. L. Clark, L. W. Pickett, and W. K. Farr, *Science,* **71,** 293 (1930).

further wall thickening.[198] In young wood cells a preferred orientation is found after the tenth day.[195] There remains a possibility, however, that these observations are subject to masking of orientation effects in early growth stages by the large quantities of water in young fibers, for even though young cotton fibers exhibit no x-ray crystallinity before drying, they are fibrillar in nature and exhibit strong birefringence. This would indicate that the cellulose is oriented at the time of deposition with the molecules separated laterally by limited layers of water.[199] In even the youngest cells of *Valonia,* an orientation which does not change with growth can be detected.[184]

It is impossible to prove conclusively the presence or the absence of selective orientation in most natural cellulosic materials except for *Valonia*[182,183] and other naturally occurring cellulose sheets,[200] but it has been postulated for other fibers.[8] Sisson[188] has shown theoretically that if the (101) plane of a cellulose crystallite were oriented parallel to the fiber surface, the two 101 arcs would remain on the equator of the x-ray diagram, while the $10\bar{1}$ and 002 arcs would split into four arcs on either side of the equator as the spiral angle increased. If, however, the fibrils were rotated at random or twisted around their own axis, then as the spiral angle increased all three equatorial arcs would divide and move toward the meridian. Sisson then found that all the cellulose fibers examined which had a large spiral angle gave x-ray diagrams characteristic of the second case, or nonselective orientation. The data for fibers of medium spiral angle such as cotton and sisal also indicated nonselective orientation but much less definitely than for large angles. By implication, the orientation of the more perfectly oriented fibers such as ramie, flax, and hemp might be considered nonselective, but from the data no definite conclusions can be made.

(b) **Orientation in Regenerated Cellulose Fibers.** For regenerated cellulose fibers the various types of orientation will be used as previously defined for native fibers. These types will be illustrated by drawings of the unit cell arrangement and the corresponding x-ray diagram as shown in Figure 22. The usual method of producing orientation in a regenerated fiber is by stretching, which produces an alignment of the major crystallographic axis parallel to the direction of stretch. The cellulose crystallite also possesses a secondary orienting tendency, as shown by the fact that a minor axis (101) of the crystallite is oriented perpendicular to the direction of shrinkage when swollen cellulose is dehydrated.[201] Since shrinkage always occurs during the formation of a regenerated fiber, it is necessary to consider the orientation of both the long axis of the crystallite and the (101) plane as affected by dehydration and by stretching. The orientation of the unit cell of the crystallite is located by the *b* axis (direction of the cellulose chain and by the (101) plane which is shaded in the drawing (Fig. 22).

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[198] E. E. Berkley, *Textile Research,* **9,** 355 (1939).

[199] E. E. Berkley and T. Kerr, *Ind. Eng. Chem.,* **38,** 304 (1946).

[200] H. Mark and G. von Susich, *Z. physik. Chem.,* **B4,** 431 (1929).

Regenerated cellulose, when first formed, is usually in a highly swollen condition. Upon dehydration, either by chemical agents or by drying, considerable shrinkage in volume takes place and, simultaneously with this shrinkage, orientation is produced. The type of orientation is governed by the direction of shrinkage, and the degree of orientation by the degree or magnitude of this shrinkage. The effects of shrinkage on orientation as detected by x-ray measurements are summarized in Figure 23.

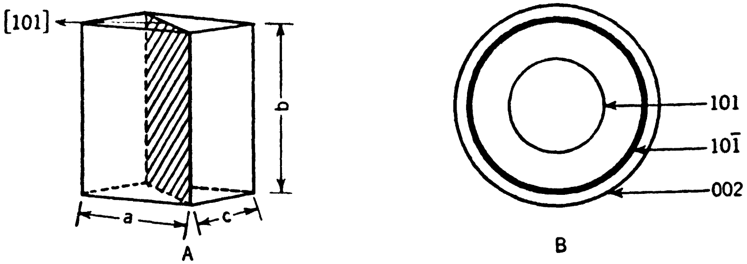

Fig. 22. Unit cell arrangement and x-ray diagram of celulose II (Sisson[201]) (A) Schematic representation of the unit cell showing unit cell axes and the (10$\bar{1}$) plane, which is shaded; (B) x-ray diagram of cellulose II showing the location of 101, 10$\bar{1}$, and 002 diffraction rings.

If a swollen cube of cellulose shrinks along one axis (Figure 23 AE), the (101) planes are oriented perpendicular to the direction of shrinkage, but there is random arrangement of the *b* axis about this direction. This type of orientation produced by shrinkage along one axis may be classified as a selective uniplanar orientation.

If shrinkage takes place in two directions (Fig. 23 AF), the *b* axes of the unit cells are oriented parallel to the axis which did not shrink, but the crystallites have random orientation around the *b* axis. This type of orientation resulting from shrinkage along two axes is a uniaxial orientation. If shrinkage takes place in all three directions (Fig. 23 AG), the crystallites have a random orientation when viewed from any direction.

Swollen coagulated cellulose can also be deformed by tension or pressure

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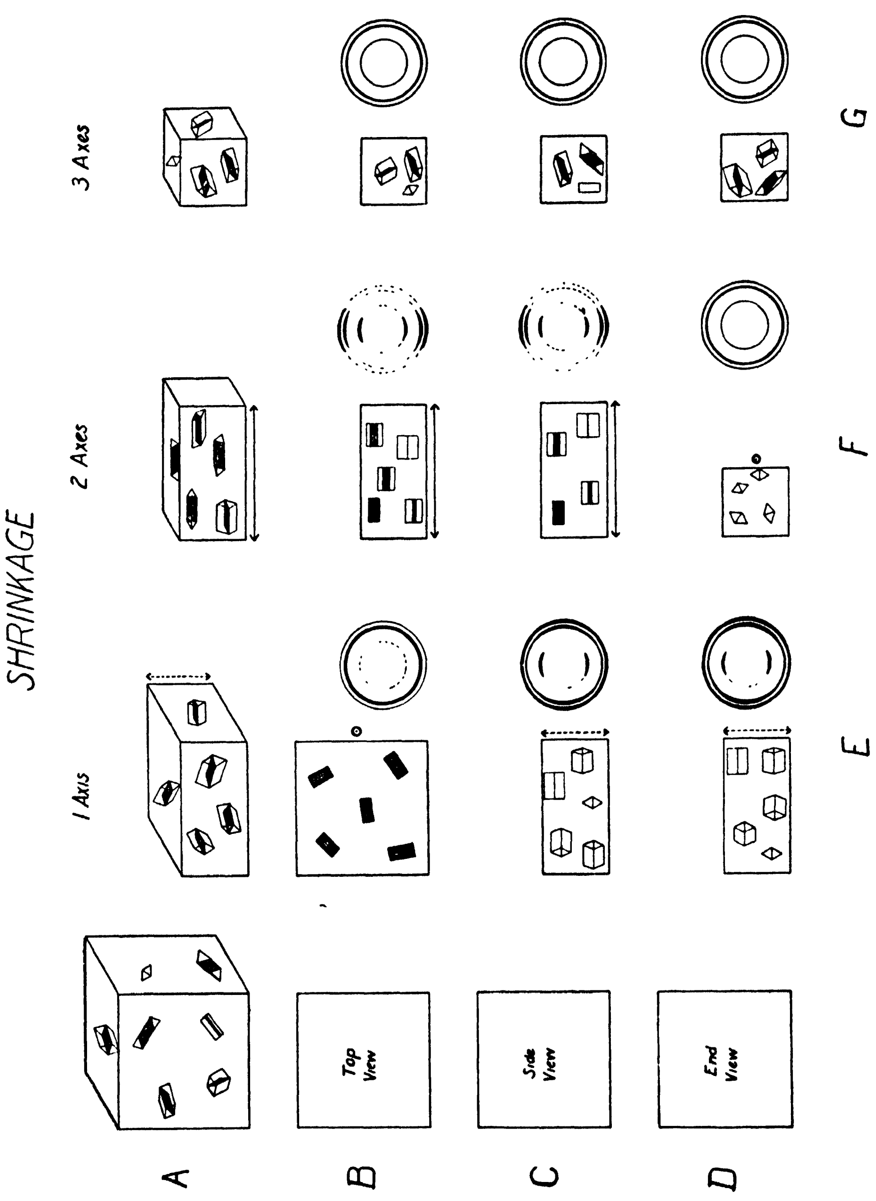
[201] W. A. Sisson, *J. Phys. Chem.*, **44**, 513 (1940).


SHRINKAGE
1 Axis
2 Axes
3 Axes
A
B
C
D
E
F
G
Top View
Side View
End View

(*See legend on opposite page*)

to produce a preferred orientation. The effects of deformation by elongation or contraction are shown graphically in Figure 24 in the same manner as the effects of shrinkage are shown in Figure 23. It is difficult to evaluate the effects of shrinkage and deformation separately, since the two always act collectively in producing the dry sample necessary for x-ray analysis. The most tangible factor for correlation with orientation produced by combined deformation–shrinkage effects is again the relative changes in sample dimensions. In terms of these changes, the following general conclusions may be drawn: whenever there is a relative increase in dimension in one direction, the *b* axes of the crystallite tend to orient parallel to this direction; if there is a relative decrease in dimension in one direction, the (101) planes tend to orient perpendicular to that direction.

The results obtained by either shrinkage or deformation may be summarized as follows: a random orientation is present in the original swollen sample or is produced by shrinkage along three axes; uniaxial orientation is produced by shrinkage along two axes, or by elongation on one axis and shrinkage along two (Fig. 24AF); uniplanar orientation is produced by shrinkage along one axis or by elongation along two axes and shrinkage along one (Fig. 24AG); and biaxial orientation is produced by shrinkage along one axis and elongation along one axis (Fig. 24AE). The degree of orientation in each case is proportional to the relative magnitude of the dimensional changes in the sample. After a given type of orientation is formed, it is possible in some instances to change from one type to another. For example, if a uniplanar sample is stretched, it is first changed into an imperfect biaxial and eventually into a uniaxial orientation.

In the industrial production of rayons, deformation is usually followed by or produced simultaneously with shrinkage; the two factors may either reinforce or oppose one another, thus complicating the situation and making it difficult to evaluate the factors which influence the production of orientation. Many early workers assumed that the orientation present in rayon

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←Fig 23. Schematic representation of types of orientation and corresponding x-ray diagrams obtained when swollen regenerated cellulose shrinks along various axes (Sisson[201]). A cube of swollen coagulated cellulose having random orientation is schematically represented in the upper left-hand corner. The types of orientation obtained when the cube shrinks along different axes are shown in the vertical columns E, F, and G. The corresponding x-ray diagrams are shown with the sketches. The horizontal columns A, B, C, and D show the orientation and x-ray diagrams when viewed from different directions. Arrows indicate the fiber axis direction; solid lines represent major axis orientation (*b* axis of unit cell); and dotted lines represent minor axis orientation (normal to (101) plane). Thus, Figure 23BE refers to the orientation produced by shrinkage in one direction when viewed along the axis of shrinkage.

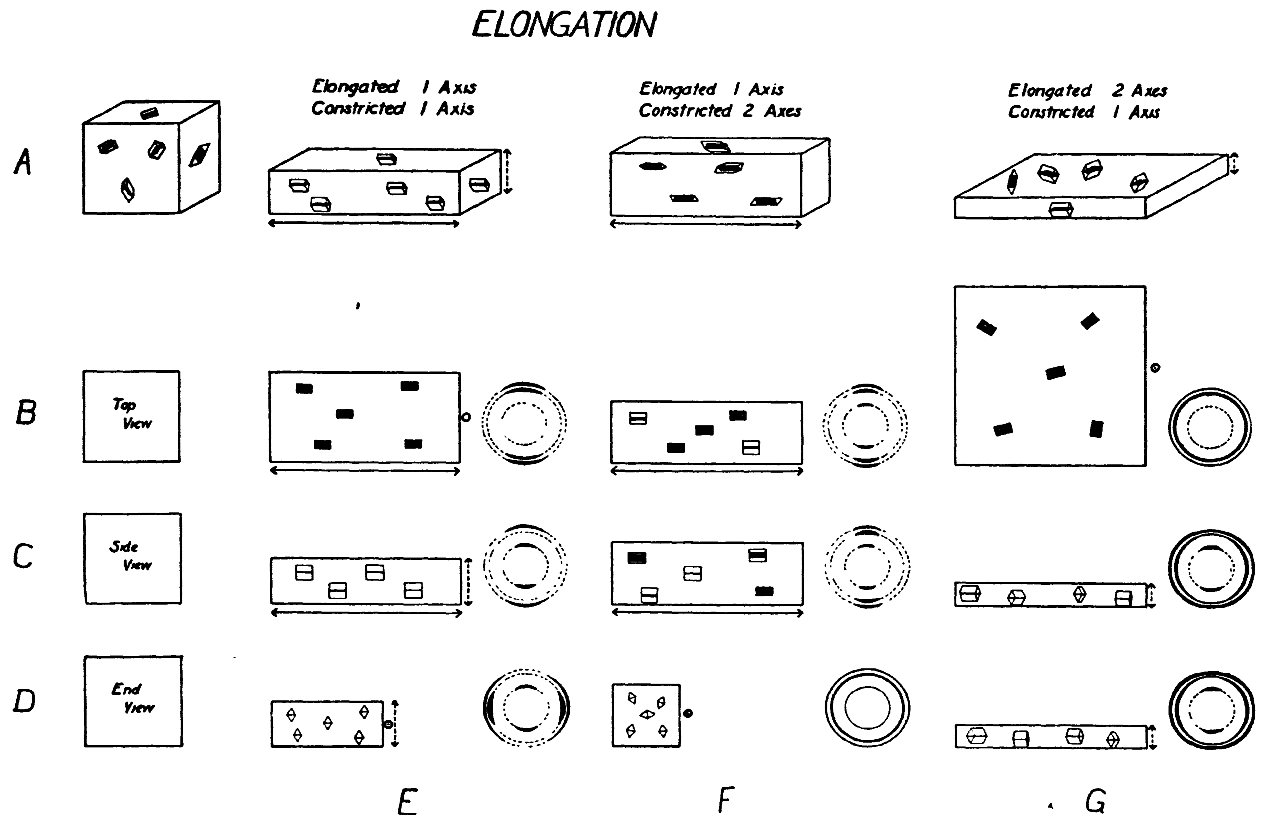
ELONGATION
Elongated 1 Axis
Constricted 1 Axis
Elongated 1 Axis
Constricted 2 Axes
Elongated 2 Axes
Constricted 1 Axis
A
B
C
D
Top View
Side View
End View
E
F
G

Fig. 24. Schematic representation of the types of orientation produced and the x-ray diagrams obtained when swollen regenerated cellulose is deformed along various axes (Sisson[201]) The results are represented in the same manner as in Figure 23.

filaments was produced before coagulation while the viscose was passing through the spinneret, and that the role of the coagulating agent was primarily to fix the orientation already present. Although orientation may be produced in the spinneret, as evidenced by streaming double refraction of viscose passing through an orifice, it now seems probable that the degree and type of shrinkage or elongation are the most important factors in producing the final orientation of the rayon.[201] The composition and length of the spinning bath, the rate of spinning, and the filament diameter and shape all have a pronounced influence on the ultimate type and degree of orientation.[45] It is possible that these factors influence orientation principally indirectly by varying the degree of swelling or rate of shrinkage at some critical time in the coagulation process[201,202] but the mechanisms involved are not fully understood. There seems no doubt, however, that the orientation is determined principally during coagulation and resulting shrinkage of the fibers while in the spinning bath and by stretch on the swollen gel, for little or no change in orientation occurs during the drying of filament after it has been essentially dehydrated in the bath.[202,203]

In Figure 25 there is represented schematically the cross section (Fig. 25AD), orientation (Fig. 25BD), and the x-ray diagram (Fig. 25CD) of a swollen rayon fiber. Although shrinkage along one axis could occur in either the longitudinal, tangential, or radial direction, only the latter possibility will be considered. Since the circumference does not change, the cross section could assume any shape between the serrated type (Fig. 25AE) common in modern rayons and a flat ribbon shape. As previously pointed out, radial shrinkages should produce a selective uniplanar orientation with the (101) planes parallel to the filament surface and the *b* axes randomly arranged in planes parallel to the surface. With the x-ray beam perpendicular to the fiber axis, the 101 line should exist as equatorial reflections and the $10\bar{1}$ line as complete circle (Fig. 25CE).

In the case of shrinkage of the rayon fiber along two axes, there are also three possibilities, only one of which, shrinkage in the radial and tangential directions, is represented (Fig. 25AF). This produces uniaxial orientation with the *b* axes parallel to the fiber axis; all three planes diffract on the equator (Fig. 25CF). Shrinkage along three axes (Fig. 25AG) can occur in only one way to produce a random orientation.

In the case of elongation, rayon fibers can be stretched only in one direction parallel to the fiber axis and all such stretch tends to produce uniaxial

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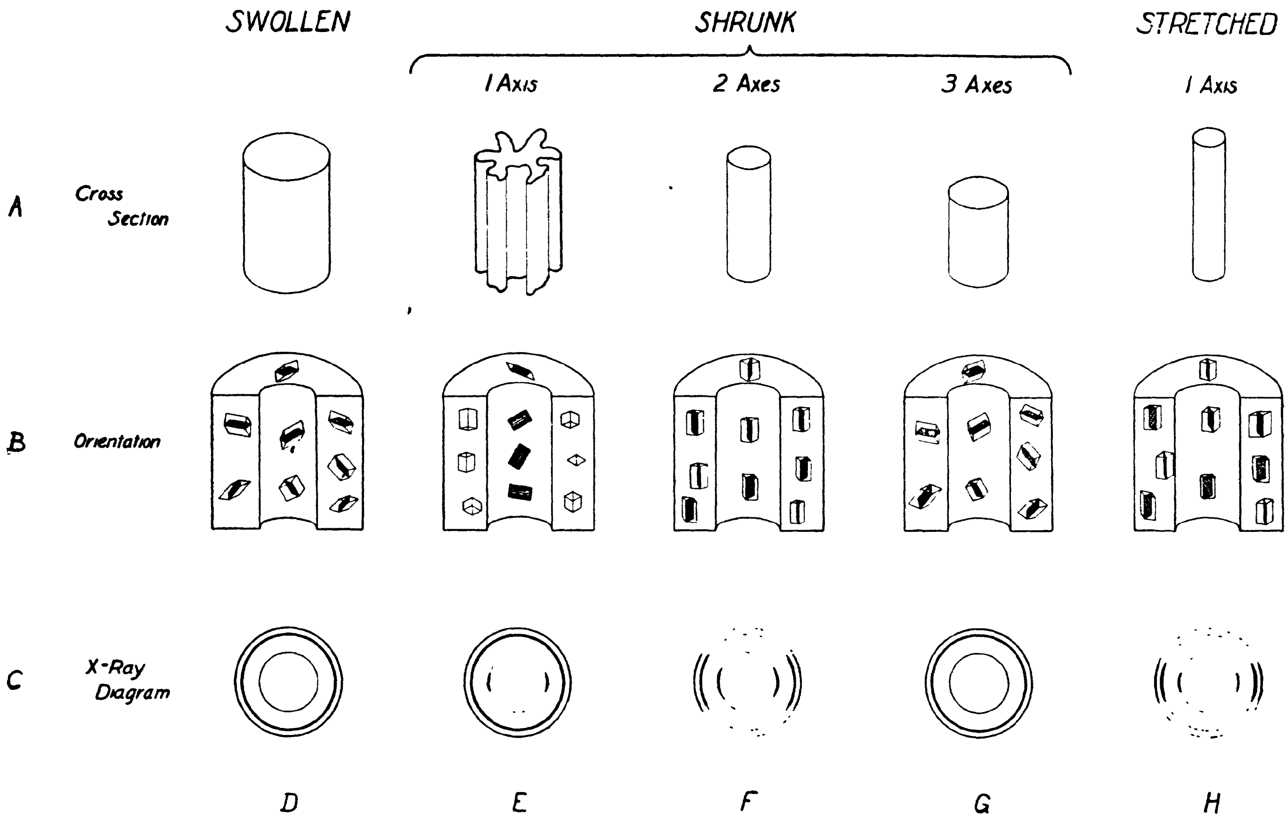
[202] P. H. Hermans, J. J. Hermans, D. Vermaas, and A. Weidinger, *J. Polymer Sci.*, **2**, 632 (1947).

[203] P. H. Hermans, O. Kratky, and R. Treer, *Kolloid-Z.*, **96**, 30 (1941).



SWOLLEN
SHRUNK
STRETCHED
1 Axis
2 Axes
3 Axes
1 Axis
A
Cross Section
B
Orientation
C
X-Ray Diagram
D
E
F
G
H

Fig. 25. Schematic representation of cross section, type of orientation, and x-ray diagram obtained when rayon filaments shrink along various axes (Sisson[201]).

orientation (Fig. 25AH). In practice, however, any combination of the seven shrinkage possibilities may have begun to occur or may be in the process of occurring while elongation is taking place. This results in such a large number of possible methods of producing orientation in rayon spinning that complete discussion cannot be given and, in fact, exhaustive studies of these phenomena have not yet been published. Krebs[204] has correlated orientation with the extent of deformation at various positions on a rayon spinning machine. Other investigators[45,205] have shown that the orientation produced by a given elongation deformation varies with viscose and bath composition and other spinning variables, and that the effect of this orientation on the ultimate properties of rayon fiber is a complex function of the sequence and magnitude of the various shrinkages and deformations occurring during spinning. The exact mechanisms involved have not been clearly defined.

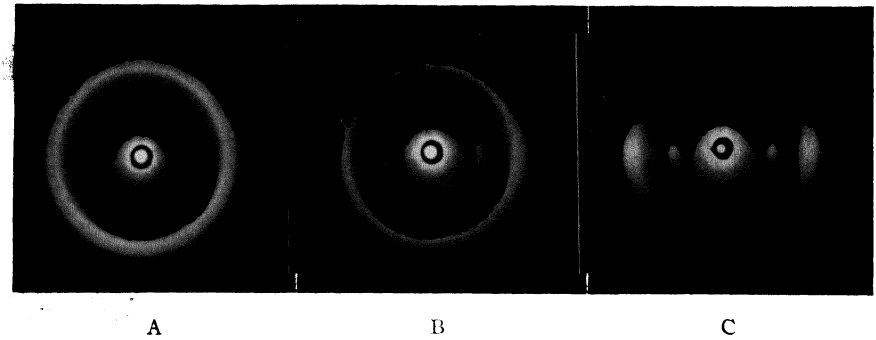


Fig. 26. X-ray diagrams of viscose fibers spun under various conditions (Sisson[201]). (A) Allowed to shrink freely; (B) not allowed to shrink in length; (C) stretched and dried under tension.

Each type of orientation illustrated in Figure 25 has been produced experimentally. Figure 26A is the x-ray diagram of a viscose rayon spun and allowed to dry without tension. All the diffraction lines show random orientation (Fig. 25CG). Figure 26B is the diagram of a fiber spun under the same conditions with the exception that the ends of the fiber were clamped immediately after coagulation so that longitudinal shrinkage was prohibited. The 101 line shows some orientation, whereas the $10\bar{1}$ and 002 lines show the random orientation characteristic of selective uniplanar orientation (Fig. 25CE) which should result if shrinkage were confined to the radial direction. This diagram is typical of x-ray diagrams of earlier types of viscose rayon. Figure 26C is the diagram of a rayon fiber which was stretched and dried under tension. All the diffraction lines exist as the equatorial maxima characteristic of uniaxial orientation. This type of orientation is characteristic of most modern rayon fibers, especially those of high-tenacity rayons. If the rayon in Figure 26B is moistened and slowly stretched, the selective orientation is slowly changed to a uniaxial orientation. The effect of plasticizers, such as water, in assisting orientation is illustrated by the fact that, although stretching dry rayon may increase the preferred orientation, the magnitude of the increase is always much lower for a given degree of deformation than for the same fiber stretched in the wet state.

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[204] G. Krebs, *Kolloid-Z.*, **98**, 200 (1942).

[205] P. H. Hermans, *Contributions to the Physics of Cellulose Fibres*, Elsevier, New York, 1946, pp. 166–175.

Regenerated cellulose sheets such as cellophane usually exhibit a selective uniplanar orientation.[201] This type of orientation is produced by shrinkage along one axis (Fig. 23AE) or by elongation along two axes and shrinkage along one (Fig. 24AG). It may be anticipated since the principal shrinkage takes place perpendicular to the plane of the sheet in the usual commercial method of producing cellophane. In commercial cellophane sheets, the above orientation may vary in degree of perfection of the selective orientation of the (101) planes or in preferred orientation of the *b* axes in the plane of the sheet. The latter case is an imperfect biaxial orientation and may occur near the edge of the sheet.

Selective orientation similar to that found in cellophane is also found in specialty rayons spun in such a manner that the filaments are flat and ribbonlike.[206] Because of the shape of the filament, the shrinkage during coagulation is essentially unidirectional perpendicular to the large surface of the filament, and the (101) planes are arranged perpendicular to this direction. Since most rayons are elongated along the fiber axis during production, there is some tendency for the *b* axes of the crystallites to be oriented parallel to the fiber axis, and the orientation in these flat filaments is selective uniplanar with a tendency toward biaxial orientation.

(3) *Relationship of Orientation to Physical Properties*

The influence of orientation on the physical properties of cellulose has been discussed by many investigators, particularly with reference to the tensile strength, elasticity, classification, and dyeing properties of cotton, the density, tensile strength, expansion, and shrinkage of woods, and the

[206] A. N. J. Heyn, *Rayon and Synthetic Textiles*, **31**, 39 (Sept. 1950).

tensile strength, elongation, swelling, and dyeing of rayon fibers. Complete details of all these studies are beyond the scope of this discussion, but the reported effects of increasing orientation are listed in Table 12 and illustrated by the examples which follow.

TABLE 12

Effect of Increasing Orientation on Some Fiber Properties

Increases	Decreases	Little or no effect
Tensile strength	Total elongation	Sorption of water
Transverse swelling	Reversible elongation	Elastic limit
Recovery after wet stretching	Longitudinal swelling	
Young's modulus	Dye absorption	
Rigidity	Plasticity	
Refractive index	Crease resistance	
Gloss	Chemical reactivity	

In ramie the cellulose crystallites are oriented almost parallel to the fiber axis. As a result, ramie fibers have very high tensile strength, but they are brittle and weave into a relatively harsh fabric. Perfect alignment thus contributes great strength and rigidity in the fiber direction and brittleness in the transverse direction. In cotton the crystallites are inclined at an angle to the fiber axis; thus cotton does not have the tensile strength of ramie, but it is more resilient and weaves into a softer fabric.

By using a quantitative x-ray method for measuring orientation, close linear correlation can be obtained between orientation and tensile strength of raw cotton[176,177,179,186] as shown in Table 13. This orientation—strength relationship may be different for different species of cotton or for different varieties within a species. For example, sea island and American-Egyptian cottons are usually stronger for a given x-ray angle than American upland

TABLE 13

Relationship of Cotton Strength to X-Ray Orientation (Sisson[179])

Tensile strength, lb./sq. in.	X-ray angle, degrees	Tensile strength, lb./sq. in.	X-ray angle, degrees
111,900	24.2	84,000	38.5
105,000	23.2	82,700	37.3
92,200	30.5	80,000	37.5
92,000	34.1	72,900	42.6
84,400	35.6	71,900	43.0

varieties. Environmental factors do not usually affect this relationship.[177]

Woods which have a parallel orientation are those which split easily and have high tensile strength and low longitudinal shrinkage. With more random orientation or pronounced spiral orientation, the wood is tougher but the tensile strength is lower and the shrinkage high.[195,196] Thus, summerwood usually has higher orientation than springwood and is marked by high tear strength and low burst strength.[191,193] However, the difference in cell-wall thickness between summerwood and springwood probably has more influence on the properties of wood than do the differences in orientation (see Chapter V-A).

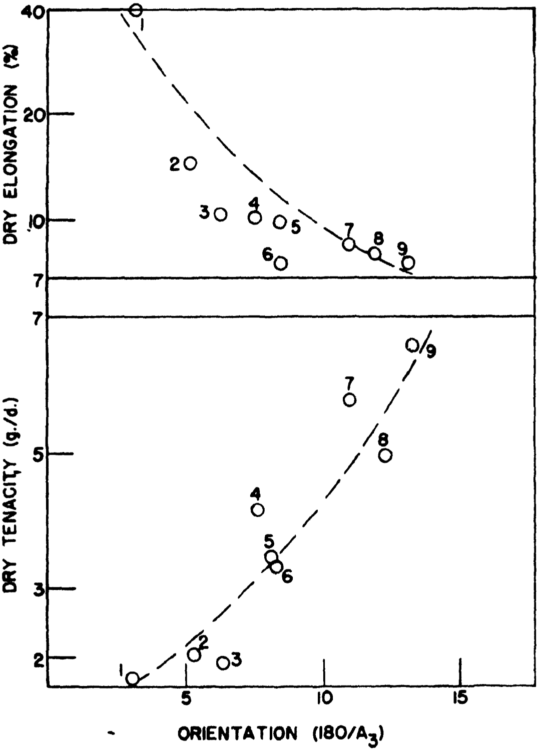

Fig. 27. Dry tenacity and dry elongation as functions of orientation for standard rayons (Ingersoll[45]). Points: (1) Fiber D; (2) textile rayon; (3) Bemberg; (4) Cordura 237; (5) Cordura 133; (6) Lilienfeld; (7,8) Fiber G-2; (9) Fortisan. 180/A$_3$ = fraction of semicircle occupied by the 002 diffraction arc.

The tenacity–elongation–orientation relationships for standard rayons and some experimental rayons are shown in Figures 27 and 28, respectively. As a general rule, the tenacity increases linearly while elongation decreases hyperbolically with increasing orientation. The scatter of the data in Figure 27 indicates that factors other than orientation also affect these properties. In considering the effects of orientation on the properties of rayons, it is indeed difficult to isolate crystallinity or lateral order from orientation since both occur during spinning and each influences the production of the other. No sweeping generalizations can be made, therefore, and the curves in Figure 27 represent the highest tenacities and elongations so far observed at these orientations. These values correspond to the tenacity and elongation a given yarn should develop if it is as efficient as the refer-

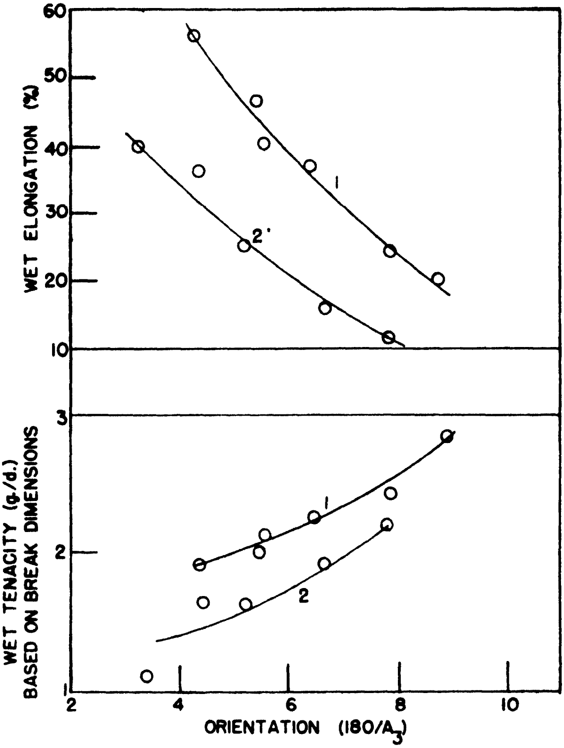

Fig. 28. Wet tenacity and wet elongation as functions of orientation for experimental rayons (Ingersoll[45]). Curves: (1) Acid–sulfate–zinc bath yarns differing only in stretch; (2) acid–sulfate bath yarns differing only in stretch. $180/A_3$ = fraction of semicircle occupied by the 002 diffraction arc.

ence yarns in converting orientation into physical properties.[45] Thus, it is possible to obtain two rayons which have the same degree of orientation but widely different physical properties as shown in Figure 28; the yarns spun in acid–sulfate–zinc baths have both a higher tenacity and higher elongation at a given orientation than those spun in acid–sulfate baths. In these cases, when a rayon having a low tenacity does not show a corresponding high elongation, the low tenacity must be attributed to factors other than orientation. These same phenomena have been noted for viscose and cuprammonium fibers. The viscose rayons usually exhibit higher tenacities and higher elongations at a given orientation than cuprammonium rayons.

It is difficult to define all the other factors which influence the relationships between orientation and physical properties but for the most part these factors are of two types: (1) mechanical nonuniformities and (2) structural variables other than orientation. In the case shown (Fig. 28) an explanation is possible on the basis of structural variations. The acid–sulfate–zinc yarns usually have a lower lateral order[45,46] than acid–sulfate yarns. As previously pointed out, both tenacity and elongation have been observed to decrease with increasing lateral order and the differences shown can probably be principally accounted for by the higher lateral order of the acid–sulfate yarns.

Ingersoll[45] pointed out that in some cases physical properties may vary even at constant orientation and lateral order and, therefore, that still other structural factors must be operating. The most prevalent concept concerning these other factors defines them principally as variations in the distribution of lateral order and orientation in a given fiber. Thus, as discussed previously, one would expect a yarn with a uniform single-peak lateral-order distribution to exhibit better physical properties than one with an extremely nonuniform distribution if for no other reason than that applied stress would be distributed more evenly across the fiber. Reasoning similar to that used for lateral-order distribution can be applied to orientation distribution so as to construct curves of orientation versus order. This treatment can not be made rigorous because (1) the orientation of molecules in high-order regions is a function of the orientation of these regions which is a distribution in itself and must be represented by an average value, and (2) the orientation at low order is essentially molecular orientation within the low-order region rather than the orientation of the region itself. However, the basic generalizations can be made that given fibers may have high orientation in high-order regions and low orientation in low-order regions or other combinations of these variations, and that the physical properties of systems of high order–high orientation, low order–low orientation will be different from those of high order–low orientation and low order–high orientation.

Although very few quantitative orientation studies are comprehensive enough to allow exact evaluation in this manner, tentative orientation–order curves are shown for a few fibers in Figure 29. These curves can be considered only as first approximations and are based upon optical and x-ray orientation measurements and many observations in the authors' laboratories of properties of rayons of known structure.

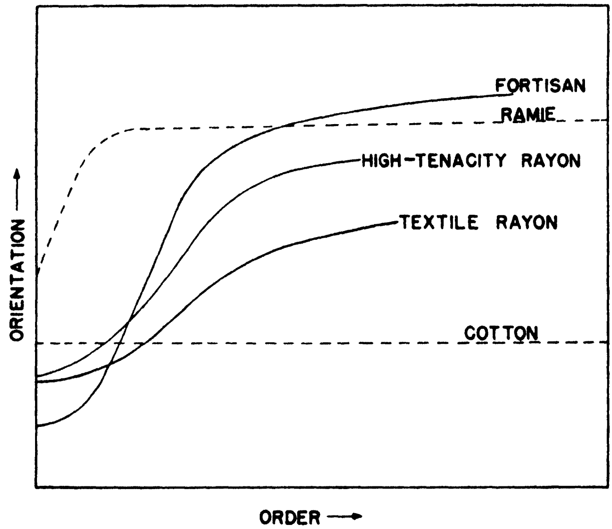

Fig. 29. Tentative lateral order–orientation curves for cellulose fibers.

Hermans[202,207] postulated that since optical orientation factors are dependent on the whole fiber substance and x-ray orientation measurements are dependent on the crystalline regions only, the ratio of the two factors should be indicative of the relative crystalline–amorphous orientation and that the ratio will be unity at equal orientations in both crystalline and amorphous regions. By actual measurement, he found that in general the optical factor is much lower than the x-ray factor; the two factors approached one another with increasing orientation, and were practically identical in rayons prepared by processes involving high swelling during

[207] P. H. Hermans, *Physics and Chemistry of Cellulose Fibres*, Elsevier, New York, 1949, pp. 261, 454–461.

orientation, such as Lilienfeld or Fortisan rayon. He concluded that the movements of the amorphous and crystalline components during deformation were always of the same nature and that the difference between crystalline and amorphous orientation became relatively small at high degrees of orientation. This would imply that, contrary to the theory discussed above, a yarn with high crystallite orientation will also have high orientation in the amorphous regions. Dart[208] has found, however, that if optical orientation is measured by an optical method involving light transmitted through a single filament, the resulting orientation factor is always much lower than the optical factor measured on a fiber surface. This implies that the amorphous orientation is actually lower than that found by Hermans. At the present time, no definite choice can be made between these concepts. However, since many reversible phenomena observed in wet stretching and drying under tension of rayon yarns and subsequent rewetting and relaxed drying seem most compatible with a metastable orienting and subsequent disorienting of low-order regions without appreciable change in crystallite orientation, the orientation of low-order cellulose has been set below the values indicated by Hermans' work.

The treatment illustrated in Figure 29 is more adaptable to regenerated fibers than to native fibers except for those fibers of essentially parallel orientation. Thus, the fibrillate nature of the cotton fiber is such that it must be treated as a bundle of fibers with the result that in respect to the fiber axis, no distinction can be made between orientation at various levels of order. The curve shown can only be taken as an indication of the level of orientation in cotton fibers and is given merely for comparison.

2. Cellulose Fiber Reactions

The following discussion of cellulose fiber reactions will not be concerned to any great extent with the chemistry of cellulose reactions, for such material is presented in Chapter IX-A. The discussion will instead be directed toward the structural principles involved, that is, the role of cellulose structure in determining the course of reactions and the mechanisms involved, and the extension of structural concepts to cellulose derivatives. Thus, the studies of the changes in structure occurring during reaction give information regarding the mechanism of the reaction as well as the structure of the reaction product. The discussion will be principally concerned with swelling and structure phenomena and cellulose derivative formation.

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[208] S. L. Dart, private communication.

(a) SWELLING OF CELLULOSE FIBERS

Swelling is a characteristic which is closely associated with most cellulose reactions and with most stretching and forming operations necessary for the production of strong regenerated films and fibers. According to Katz[209] a solid is said to swell when it imbibes a liquid while at the same time (1) it does not lose its apparent homogeneity, (2) its dimensions are enlarged, and (3) its cohesion is diminished; that is, it becomes soft and flexible.

Solids which can undergo swelling are, in a great many cases, substances of high molecular weight. Furthermore, many of these solids consist of a large number of discontinuous crystalline regions which are separated by regions of lower crystallinity, and are usually composed of macromolecules containing polar groups capable of forming fairly strong interchain bonds. The swelling behavior of these solids is frequently dictated to a great extent by this interchain bonding. As a general rule, liquids or vapors which cause swelling must be capable of breaking these secondary bonds between molecules and of forming their own bonds with the polymer. As a corollary, it follows that in any solid containing both crystalline and amorphous regions, it will be more difficult for the swelling liquid to disrupt the dense hydrogen bond network of the crystalline regions than to disrupt the weaker bond network of less crystalline regions. Cellulose fibers, as high molecular weight solids in which the molecules are held together by at least three types of bonds (van der Waals forces, polar hydrogen bonds, and primary valence bonds), fulfill all the conditions for complex swelling and associated phenomena.

(1) Types of Swelling

On the basis of x-ray diagrams of swollen cellulose, Katz[209] has defined two principal types of swelling as "intermicellar" and "intramicellar" swelling. In the present discussion these will be referred to as "intercrystalline" and "intracrystalline" swelling, respectively. In intercrystalline swelling, the swelling reagent penetrates only the intercrystalline amorphous regions. It is marked by the fact that there is no change in the x-ray diagram except for the superposition of the diagram of the swelling reagent on the cellulose diagram. In intracrystalline swelling, the swelling agent penetrates the interior of the crystalline as well as the intercrystalline material. The x-ray diagram of the solid changes during swelling. From these changed x-ray diagrams it is possible to distinguish two cases of intracrystalline swelling: (1) the lateral intermolecular distances change continuously as a function of the degree of swelling; and (2) the original cellulose x-ray diagram gradually decreases in intensity and a new diagram is formed as swelling proceeds. In this latter case it is generally assumed that the swelling reagent forms a compound with cellulose and that the original crystal unit cell structure is changed to a new unit cell structure characteristic of the compound. The nature of this compound formation will be discussed later.

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[209] J. R. Katz, *Trans. Faraday Soc.*, **29**, 279 (1933).

Intercrystalline and intracrystalline swelling may both be subdivided further into limited and unlimited swelling. Limited swelling may be said to occur when there is a maximum to the amount of liquid taken up, whereas unlimited swelling usually results in solution of the cellulose. Thus, dispersion may be considered a condition of unlimited swelling and on the basis of the two types of swelling, intercrystalline and intracrystalline, it is theoretically possible to have either "micellar" or molecular dispersion. For molecular dispersion both types of swelling must be unlimited; for micellar dispersion, intercrystalline swelling should be unlimited and intracrystalline swelling either absent or limited. Actually, dispersion from intercrystalline swelling alone seldom occurs unless the swelling reagent is also a strong hydrolyzing or oxidizing agent so that a dispersion may result as a result of degradation.

The type and extent of swelling for any given condition depend upon the nature of the swelling reagent, its specific interaction with cellulose, and the nature of the order–disorder structure of the cellulose sample. All of these factors will be treated in the following discussion, but in view of the general nature of swelling phenomena a complete discussion of the swelling by various solvents is impossible and each type of swelling will be discussed in terms of common examples.

(2) *Intercrystalline Swelling*

The best example of cellulose intercrystalline swelling is the swelling of cellulose fibers in water. As soon as water sorption begins the fibers start to swell; the swelling increases in regular fashion as the total sorbed water increases with increasing relative humidity and attains its maximum value on immersion of the fiber in excess water.[210] The total volume of the system increases with increasing swelling in such a manner that as a first approximation each water molecule entering the fiber can be assumed to contribute its normal molecular volume to the system.[211] The magnitude of the swelling varies from fiber to fiber as shown by the fact that the maximum increase in cross-sectional area on swelling in water is 20–35% in natural fibers and 55–70% in regenerated fibers.[210] Although slight changes in x-ray diagrams may occur on wetting,[50] especially in low-order systems, there seems little doubt that this swelling is chiefly intercrystalline.

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[210] F. F. Morehead, *Textile Research J.*, **17**, 96 (1947); **22**, 535 (1952).

[211] H. J. White, Jr., and H. Eyring, *Textile Research J.*, **17**, 523 (1947).

Organic liquids in general swell cellulose less than water, the swelling being chiefly dependent on the polarity and molecular volume of the liquid. Thus, methanol swells cellulose less than does water; with increasing molecular weight the swelling by normal alcohols decreases until it becomes negligible in *n*-butanol. Swelling in benzene is negligible,[212] but a series of benzene derivatives give increased swelling in the order $CH_3 < NH_2 < CHO < Br < Cl < NO_2$. This order is the same as that of increasing dipole moment of the liquids.

Swelling beyond the water-swollen dimensions takes place when cellulose is immersed in certain aqueous solutions of acids, bases, or salts. The order of swelling power of the salts follows the well-known lyotropic series, the more hydrated ions being the most effective swelling reagents. The decreasing order of swelling for various cations and anions is as follows[213]:

$$\mathrm{Zn > Li > Ca > Mg > Ba > Na > NH_4 > K}$$
$$\mathrm{CNS > I > PO_4 > Br > Cl > NO_3 > SO_4 > ClO_3}$$

Swelling beyond the water-swollen condition is also caused by aqueous solutions of various organic compounds such as thiourea, chloral hydrate, resorcinol, and benzenesulfonates.[209]

As a general rule, a cycle of intercrystalline swelling and subsequent deswelling by removal of the swelling reagent does not affect the network structure to any great extent unless the structure has been set in some metastable state by some extreme condition during its formation or some other factor such as temperature has been varied. For example, a strained rayon fiber which has been stretched while wet and dried under tension will shrink irreversibly on subsequent wetting and relaxed drying. The straining operation induces a metastable state of higher molecular orientation and induces higher order by interchain bonding in various low-order regions. When these regions of short-range order are disrupted by swelling, relaxation occurs and the total order in these regions is decreased. "Amorphous" cellulose produced by dry-grinding[54,55] crystallizes readily on swelling in water, and this crystallization continues on drying. This is apparently a special case in which the normal network restraints on swelling are

[212] A. J. Stamm, *Ind. Eng. Chem.*, **27**, 401 (1935).

[213] A. J. Stamm, U.S. Dept. Agr., *Misc. Pub.* **240** (1936).

not active because of severe degradation during grinding. Rayon yarns heated at elevated temperatures in the presence of water vapor can also be crystallized slightly.[214] This effect is comparable to reordering cellulose esters by heat and swelling reagents; that is, the swelling increases chain mobility in the swollen regions and allows reordering not possible at low temperatures. The total crystallization possible is extremely limited unless the network is disrupted by degradation.

Although the total swelling produced by a given liquid in a number of cellulose fibers decreases with increasing order, no generalization to this effect is possible. The total swelling of a given system is more directly related to the network structure of the fiber—that is, the distribution of order as outlined previously, the size and order within amorphous regions, and the size and order within the crystalline regions—than to a given crystalline–amorphous ratio. A fiber in which the network is composed of large, perfect, ordered regions and large, imperfect, disordered regions will probably swell more for a given condition than a fiber in which the network is composed of small, relatively low-order ordered regions, and small, relatively ordered disordered regions. These two cases are most comparable to the relatively high-swelling "core" and low-swelling "skin" in rayon fibers. The total swelling is determined in each case by the extent to which the network can swell without provoking resistance to further swelling from the crystalline region "cross-links."

(3) *Intracrystalline Swelling*

In view of the present concepts of lateral-order distribution in cellulose fibers, the division of swelling phenomena into two discrete classes, intercrystalline and intracrystalline swelling, must be considered an oversimplification subject to the same arguments offered for the crystallinity simplifications discussed previously. Thus, in fibers in which the crystalline and amorphous regions differ only slightly in terms of order (as in high-tenacity rayon, Fig. 14) it is frequently difficult to distinguish between inter- and intra-crystalline swelling. Elements of intracrystalline swelling as defined by x-ray diffraction may also occur in a liquid normally considered to be intercrystalline in action for systems with marked order differences between the ordered and disordered regions (as cotton in Fig. 14). Thus, Hermans and Weidinger[50] have reported that water swelling of mercerized and rayon fibers causes a slight shift in the 101 interference of the x-ray diagrams indicating that the crystalline lattice expands about 0.5 A.

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[214] R. C. Waller, K. C. Bass, and W. E. Roseveare, *Ind. Eng. Chem.*, **40**, 138 (1948).

in this direction. This was interpreted as indicating intracrystalline swelling in water for cellulose II structures. On the basis of current views it seems more probable that this effect is merely a reflection of the gradual transition from order to disorder and the relatively large amounts of borderline order in these fibers. These borderline regions have sufficiently high order to give coherent x-ray diffraction and sufficiently low order to swell in water, and are present in sufficient quantity to be detectable. Similar regions may be present in other fibers but not detectable in x-ray diagrams because of a relatively low concentration of material in this critical order range. Thus, both intercrystalline and intracrystalline swelling are essentially similar processes differing only in degree. The extent to which either or both occur in a given system is dependent upon temperature, concentration, specific interaction between cellulose and swelling agent, and the order distribution within the fiber. The x-ray diffraction techniques normally used are not completely definitive, especially in transition intervals, but nevertheless they can be used as a reliable guide to swelling behavior and mechanisms.

Most strong acids and bases and a few salts produce both intercrystalline and intracrystalline swelling, the latter occurring only at high acid, base, or salt concentrations. The action is usually specific as to whether the swelling is limited or unlimited. When the intracrystalline swelling is limited, a definite swelling compound is formed, whereas unlimited swelling usually results in solution.

When a swelling reagent capable of intracrystalline swelling is added to cellulose, the changes occurring may be divided into three steps as indicated by x-ray diagrams. When very little swelling reagent is added, the crystalline pattern is that of the original fiber. At some intermediate concentration or range of concentrations of swelling reagent, the x-ray diagram consists of the pattern of the original cellulose and a pattern characteristic of a swollen modification. With increasing concentration, the pattern of unchanged cellulose diminishes in intensity until only the pattern of the swollen modification remains. The last step may take one of three courses with increasing concentration: (1) the diagram may change continuously with swelling reagent concentration until solution results (unlimited intracrystalline swelling); (2) the diagram of the swollen cellulose may indicate a crystalline structure as well defined as that of the original cellulose and remain unchanged with further addition of swelling reagent (limited intracrystalline swelling); or (3) the sharp diagram of (2) may change to a new crystalline form or begin to change continuously as in (1) on further addition of swelling reagent.

Thus, the occurrence of intracrystalline swelling is associated with a minimum concentration for each swelling reagent below which only intercrystalline swelling occurs. According to von Susich and Wolff[215] these limiting concentrations for ramie at room temperature are 8.5–9% (3.4 *M*) for LiOH, 11–12% (3 *M*) for NaOH, and 15–17% (2.8 *M*) for KOH. According to Sisson and Saner[216] the limiting concentrations for tetramethyl-, trimethyl-, benzyltrimethyl-, and dibenzyldimethyl-ammonium hydroxides are approximately 2.0, 1.9, 1.6, and 1.15 *N*, respectively, at room temperature. For some swelling reagents such as sodium hydroxide, the minimum concentration is associated with temperature; with others such as the quaternary ammonium hydroxides, temperature has little effect. As a general rule, lower temperatures allow intracrystalline swelling at lower concentrations, and the temperature effect is least for the stronger swelling reagents (e.g., solvents). With sodium hydroxide, for example, intracrystalline swelling is produced in cotton with a 6% solution at 0°C.; a 14% solution is necessary at room temperature; whereas at higher temperatures (70–80°C.) only partial swelling occurs even in 20 to 30% solutions. In cases where solution occurs on increasing temperatures above room temperatures, the process of solution can usually be attributed to increased swelling arising from simultaneous degradation which is enhanced at high temperatures.

None of these limiting concentrations can be accepted as general for cellulose. For a given swelling reagent at a given temperature both the limiting concentration and the concentration range over which partial intracrystalline swelling occurs depend upon the order–disorder structure of the cellulose, especially in regard to the distribution of ordered region size or degree of perfection. This effect has been discussed in detail in the preceding treatment of lateral-order distribution where it was shown that the ease of intracrystalline swelling decreased with increasing crystal size and/or degree of perfection and that the limiting concentrations for various celluloses increased in the order: viscose rayon, wood pulp, and cotton linters. The mechanism of swelling in terms of structure as previously discussed for sodium hydroxide can apparently be generally applied to all cases of intracrystalline swelling. The qualification must be made, however, that the sensitivity of swelling procedures in delineating various structures varies with the swelling reagent, and as a general rule the sensitivity decreases with increasing severity of swelling action or solvent power of the reagent. Thus, the concentration range over which only partial intracrystalline swelling occurs in a relatively poor solvent such as an alkali hydroxide is of the order of 3–6% whereas for a swelling agent such as sulfuric acid the range is very narrow and of the order of 1%.

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[215] G. von Susich and W. Wolff, *Z. physik. Chem.*, **A115**, 385 (1925).

[216] W. A. Sisson and W. R. Saner, *J. Phys. Chem.*, **43**, 687 (1939).

Because of the obvious importance of swelling in rendering cellulose available for reaction, most studies of swelling have been carried out above these limiting concentrations, and, as noted previously, three types of behavior have been observed. Strong acids such as 72% sulfuric acid and 83% phosphoric acid and strong complexing reagents such as cuprammonium hydroxide and cupriethylenediamine produce unlimited intracrystalline swelling before dispersion. The crystal lattice of the cellulose is expanded in a heterogeneous manner as indicated by the absence of definite lines in the x-ray diagram especially in the 101 direction. The original equatorial diffraction lines spread gradually in the form of a streak across the equator as swelling progresses, indicating an extremely heterogeneous distribution of the lateral interchain distances.

(4) *Swelling Compounds*

Intracrystalline swelling of the limited type usually results in a definite stereometrical relationship between the anhydroglucose units of the cellulose and the molecules of the swelling reagent. The product is usually referred to as a swelling compound or crystalline addition compound. The best-known example is alkali cellulose, the swelling compound formed between sodium hydroxide and cellulose. The molecules of the swelling reagent are distributed in some definite geometric pattern throughout the expanded cellulose lattice and, as a result, swelling compounds give an x-ray diagram characteristic of the swelling reagent. In the present discussion a swelling compound will be defined as a swelling product which gives a definite x-ray diagram characteristic of a crystalline substance, irrespective of the nature of the reaction between cellulose and swelling reagent.

(a) **Reagents That Produce Swelling Compounds.** Nitric acid at a concentration of about 61% reacts with cellulose to form a swelling compound which gives an x-ray diagram different from that of cellulose I.[217] On washing out the acid, the cellulose II structure is formed. Perchloric acid at concentrations between 9.5 and 10.5 *M* also forms with cellulose an addition product which shows a characteristic x-ray diagram. Below this concentration only intermicellar swelling occurs; at higher concentrations the cellulose is rapidly dissolved. Cellulose II is formed on decomposition of this compound by water.

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[217] K. Andress, *Z. physik. Chem.*, **A136**, 279 (1928).

Ammonium hydroxide does not affect the lattice structure of cellulose, but it has been shown by several investigators[33–37] that liquid ammonia reacts to form two ammonia cellulose complexes: ammonia cellulose I, which is formed at temperatures above −20° to −30°C.; and ammonia cellulose II, which is formed at lower temperatures. The decomposition of ammonia celluloses leads to various modifications of cellulose structure with variation in conditions as discussed previously.

The alkylamines (methylamine, ethylamine, and propylamine) in sealed tubes at room temperature give addition compounds similar to ammonia cellulose I.[218] Swelling compounds can also be obtained with butyl-, *n*-amyl-, hexyl-, and heptyl-amines if the cellulose is preswollen with ethylamine and then transferred to the higher amine. Cellulose also swells in aqueous solutions of hydrazine, ethylenediamine, and tetramethylenediamine, and at sufficiently high concentrations swelling compounds are formed.[219] The nature of the compound depends upon whether a cellulose I or cellulose II structure is used as the starting material. On decomposition, in either case the lattice structure reverts to the form present in the original sample.

The quaternary ammonium hydroxides, with the exception of choline, form swelling compounds at intermediate concentrations, for example, about 30–36% for trimethylbenzylammonium hydroxide.[216] At higher concentrations, most of these reagents dissolve the cellulose, and on decomposition of the swelling compound the cellulose II structure is always formed.

Technically, the most important of the swelling phenomena is the action of sodium hydroxide in forming alkali cellulose. This process, commonly known as mercerization, is used widely commercially and the word "mercerization" has been used in various ways in the literature. Thus in the textile industry the term is used in reference to treating cotton with sodium hydroxide and is usually associated with the increased luster and tensile strength of the resulting yarn or fabric. In the viscose industry it is used frequently in reference only to the aging of alkali cellulose. In this discussion the term mercerization is used only in a structural sense and will refer to the type of crystal lattice structure present after swelling. If the crystal structure, after removal of the alkali, reverts to the original cellulose I, the product is not considered mercerized; if both cellulose I and cellulose II structures exist, partial mercerization has occurred; if the treated sample shows only a cellulose II structure, mercerization is said to be complete (cf. Fig. 7).

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[218] W. E. Davis, A. J. Barry, F. C. Peterson, and A. J. King, *J. Am. Chem. Soc.*, **65**, 1294 (1943).

[219] C. Trogus and K. Hess, *Z. physik. Chem.*, **B14**, 387 (1931).

A great many investigations have been carried out regarding the structure and formation of the alkali cellulose swelling compounds. Only a summary will be given here with particular reference made to work of Hess and coworkers;[220–223] additional information is given in Chapter IX-D. At room temperature several alkali celluloses are formed depending on the concentration of the alkali solution. Between concentrations of about 12 and 19% NaOH, the so-called alkali cellulose I is formed. When this is dried, a new modification, designated as alkali cellulose III, is formed which will revert to alkali cellulose I on addition of water. Above 21% NaOH, a new compound, alkali cellulose II, occurs as indicated by the presence of a new x-ray diagram. If the alkali concentration in contact with alkali cellulose II is reduced, a gradual transition through alkali cellulose I occurs, and below 6% NaOH a new modification termed alkali cellulose IV appears. Sobue[224] has shown that, at low temperatures where swelling is very high, two further compounds which he called alkali cellulose VI and alkali cellulose Q may exist. Schramek and Görg[225] found that if alkali cellulose I prepared from cellulose II structures is treated with 25–28% NaOH, it is temporarily converted to still another crystal form known as cellulose V. On standing, form V gradually reverts to alkali cellulose II.

Sakurada and coworkers[226,227] have shown that when a swelling compound, such as alkali cellulose, is washed with water until free of alkali and then examined before drying, a new and sharp x-ray diagram results. This diagram indicates that the water has replaced the NaOH in the crystalline regions and represents a swelling compound known as "water cellulose." If dried in air or heated in water, "water cellulose" reverts to cellulose II and is not reversible to the "water cellulose" again except through formation of the swelling compound and subsequent washing with water. The transition from one alkali cellulose modification to another is not sharp but occurs over a range through which mixed x-ray diagrams occur, and most published data indicate that water as well as sodium hydroxide enters the

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[220] H. Sobue, H. Kiessig, and K. Hess, *Z. physik. Chem.*, **B43**, 309 (1939).

[221] K. Hess and C. Trogus, *Z physik. Chem.*, **B4**, 321 (1929); **B11**, 381 (1931).

[222] C. Trogus, K. Hess, and J. Gundermann, *Z. Elektrochem.*, **42**, 704 (1936).

[223] K. Hess and J. Gundermann, *Ber.*, **70B**, 527 (1937).

[224] H. Sobue, *J. Soc. Chem. Ind., Japan*, **43**, B24 (1940).

[225] W. Schramek and H. Görg, *Kolloid-Beih.*, **42**, 302 (1935).

[226] I. Sakurada and K. Fuchino, *Kolloid-Z.*, **77**, 346 (1936).

[227] I. Sakurada and S. Okamura, *J. Soc. Chem. Ind , Japan*, **41**, Suppl. binding, 70 (1938).

crystal lattice to form the swelling compound. These two points will be discussed in greater detail in connection with the mechanism of swelling compound formation and the significance of the various crystal modifications observed.

(b) **Crystal Lattice Modification in Swelling Compounds.** From a comparison of the lattice distances of a swelling compound with those of the original cellulose, it is apparent that the most striking change occurs in the distance between the (101) planes. This distance of 6.1 A. in cellulose I structures has been reported to increase to as much as 28.7 A. in *n*-butylamine cellulose compounds.[218] This expansion apparently allows room for the introduction of the molecules of the swelling reagent into the unit cell.

TABLE 14

Effect of Swelling Agents on the (101) Interplanar Spacing of Cellulose[214, 216, 217]

Swelling agent	Observed (101) distance, A.
Liquid ammonia	10.3–10.6
Methylamine	14.67
Ethylamine	15.72
n-Propylamine	18.48
n-Butylamine	19.73
n-Amylamine	21.92
n-Hexylamine	24.85
n-Heptylamine	28.74
Hydrazine	10.3
Ethylenediamine	12.26
Tetramethylenediamine	14.65
Tetramethylammonium hydroxide	13.0
Ethyltrimethylammonium hydroxide	13.0
Benzyltrimethylammonium hydroxide	16.5
Dibenzyldimethylammonium hydroxide	16.5

In the swelling compounds from *n*-alkylamines[218] and diamines[219] the increase in the (101) distance is proportional to the length of the swelling molecule. With the quaternary ammonium hydroxides,[216] however, the increase is not always related to the size of the swelling molecule when, for example, a methyl group is replaced by an ethyl group or when the swelling molecule contains two benzyl groups instead of one. These effects are illustrated by the (101) distances for several swelling compounds given in Table 14.

These results may be explained by assuming that the molecules of the swelling reagent have a definite orientation within the crystal lattice, and that the polar group is oriented in the direction of and forms secondary valence bonds, usually of the O—H—O or N—H—O type, with the polar groups of the cellulose molecule. The molecule of the swelling reagent must be oriented approximately normal to the length of the cellulose molecule in the hydroxyl-rich (101) crystallographic plane and, therefore, the (101) distance is proportional to molecular length. In the quaternary ammonium hydroxides, the second benzyl group in the dimethyldibenzyl compound does not appreciably increase that dimension of the molecule which arranges itself normal to the (101) plane of the unit cell, and no direct relation to molecular size is noted. This mechanism is apparently generally applicable to swelling compounds. Secondary amines with the polar group in the center of the molecular chain as in isopropylamine do not form swelling compounds, and in general such compounds also produce less intercrystalline swelling than the normal isomers.

TABLE 15

Unit Cell Structures of Swelling Compounds of Cellulose

Compound	Unit cell dimensions *a*	*b*	*c*	Angle β
Cellulose I	8.35	10.3	7.9	84°
Cellulose II	8.1	10.3	9.1	62°
Alkali cellulose I[223]	25.6	10.3	13.2	40°
Ammonia cellulose II[35]	14.5	15.2	14.5	60°
Methylamine cellulose[216]	16.4	10.3	14.76	—
n-Butylamine cellulose[216]	20.8	10.3	19.79	28°
Water cellulose[224]	10.0	10.3	9.98	52°

From the above discussion it is apparent that during swelling compound formation the cellulose molecules in their lateral expansion behave as though the structure were laminated since the unit cell expands in only one direction. This expansion in the direction perpendicular to the (101) plane (see Fig. 8) probably arises from the directional distribution of the hydrogen bonds between molecules. Apparently the first action of an intracrystalline swelling reagent is to break those hydrogen bonds between cellulose molecules in the *ab* (002) plane of the unit cell (Fig. 8). If the swelling reagent has only one polar group which forms a bond with a cellulose hydroxyl, the plane of the anhydroglucose unit rotates approximately 30° around its long axis. This shifts the plane of the anhydroglucose units from the *ab* plane to a plane bisecting the *ab* and *cb* planes so that the hydroxyl groups now lie in the (101) plane. Neither the $(10\bar{1})$ or (002) distances are markedly affected by this rotation, but the angle β decreases, usually having a value of less than the 62° found in cellulose II. Unit cell structures proposed for a few swelling compound crystalline forms are given in Table 15. There is no general agreement upon these proposed crystal structures.

This mechanism of swelling will explain the action of a swelling reagent with only one polar group per molecule in usually yielding cellulose II on removal of the swelling reagent from structures originally in either the cellulose I or II forms. The same mechanism also explains the action of bifunctional diamines in yielding the same structure, after removal, that was originally present. These latter reagents apparently form hydrogen bond "cross-links" between cellulose molecules and thus prevent rotation of the anhydroglucose units from the *ab* plane so that cellulose I structures may be re-formed. Cellulose I or slightly modified cellulose I structures may also occur after swelling reagent removal if intracrystalline swelling is incomplete or the material is swollen at elevated temperatures.

(c) **Present Status of Nature of Swelling Compounds.** No unanimity has been reached as to the structural nature of swelling compounds despite the extensive literature on the subject. At least three controversial points have been widely discussed and still exist to some extent: (1) whether swelling compounds involve chemical reaction or simple addition complexes; (2) whether more than one compound or addition complex with a given swelling reagent may exist and whether they may be justifiably expressed stoichiometrically as $(C_6H_{10}O_5)_2$ NaOH for alkali cellulose I, $(C_6H_{10}O_5)$.NaOH for alkali cellulose II, and $C_6H_{10}O_5.NH_3$ and $C_6H_{10}O_5.(NH_3)_2$ for ammonia celluloses I and II, respectively; and (3) the exact lattice configurations existing in the crystalline regions of the various compounds.

In order to clarify concepts of stoichiometric relationships in compound formation, it must be pointed out that two possibilities exist: (1) any one of the OH groups may act as a reaction site and as such may combine stoichiometrically with the complexing reagent; (2) the gross composition of a crystalline compound might have a stoichiometric relationship between the swelling reagent and anhydroglucose units. That this second possibility will actually occur is rather remote because of the well-known fact that a crystalline lattice structure may be maintained over a wide variation of composition. For example, in an incompletely substituted cellulose acetate there is no doubt of a 1:1 ratio between acetyl groups and the hydroxyl groups with which they are combined, yet the crystal lattice is substantially identical to that of the triacetate. Similar considerations must apply if an addition complex rather than a definite compound is formed with the hydroxyls.

Swelling compounds of cellulose may be assumed to form by adsorption through N—H—O or O—H—O hydrogen bonds in much the same way that water is adsorbed. A notable exception is the formation of cellulose–copper complexes in cuprammonium solutions. In the case of sodium or other alkali hydroxides, a true alcoholate in which the metal ion replaces a hydrogen atom of the cellulose may be formed; in the presence of water, however, the addition complex by O—H—O hydrogen bonds takes preference over the alcoholate structure.

On the basis of this mechanism it is possible to treat both the existence of more than one addition complex and the stoichiometric composition of these complexes by analogy to the cellulose–water system in which part of the water is adsorbed through O—H—O hydrogen bonds. The amount of water adsorbed increases continuously with increasing concentration, that is, with increasing relative humidity or actual concentration in mixtures of water and other compounds such as dioxane, and with decreasing crystalline order of the cellulose. Since the adsorption of water is principally intercrystalline the analogy is not direct except for intracrystalline swelling reagents below their limiting concentrations, and the actual phenomena involved are complicated by the swelling reagent as a third component. Thus, for aqueous solutions of swelling reagent below the limiting concentration the actual amount of reagent entering into an addition complex will increase continuously as a function of concentration and will vary with the extent of crystalline order. The lower order regenerated celluloses have been observed to adsorb more NaOH at low caustic concentrations than highly ordered cotton cellulose[228,229] in a manner completely analogous to water sorption. Both water and the swelling reagent are adsorbed in this concentration range. The relative adsorbed concentration of each is the resultant of complex equilibria involving cellulose–water, cellulose–swelling agent, and water–swelling agent interactions. Certain swelling reagents and certain cellulose structures may approach a composition indicated by some simple stoichiometric ratio such as $(C_6H_{10}O_5)_2.X$ or $C_6H_{10}O_5.X$ even though the sorption is limited to low-order material. That the adsorption is nonuniform is indicated by the fact that the x-ray diagram of unchanged cellulose is retained.

As the concentration of swelling reagent increases above the limiting concentration, penetration of the ordered regions occurs, and both water and the swelling reagent enter the lattice. The amounts of both adsorbed

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[228] G. Saito, *J. Soc. Chem. Ind., Japan,* **43,** B126, B133, B160, B194 (1940).

[229] A. Brequet, R. Viatte, and H. Perra, *Mém. services chim. état (Paris)* **34,** 153 (1948).

water and swelling reagent increase rapidly, and an x-ray diagram characteristic of the swollen crystal lattice gradually replaces that of unswollen cellulose. In the case of NaOH, further increase beyond its limiting concentration (about 13% for cotton at 20°C.) causes no change in the crystal lattice and only a slight increase in the amount of NaOH adsorbed up to a concentration of about 19–20% NaOH. This apparent constancy in both composition and packing over a wide range of caustic concentration has been taken as evidence of formation of a stable compound for which the composition has been variously reported as $C_6H_{10}O_5 . {}^1/_2NaOH$[230] and $C_6H_{10}O_5 . NaOH . 3H_2O$[224] inasmuch as a simple adsorption mechanism would be expected to result in a continuously changing composition. At least a qualitative explanation of these effects can be made, however, on a physical adsorption basis. First, it must be remembered that chemical composition data are derived from the total sample and must represent the average composition of both amorphous and crystalline regions whereas the x-ray data pertain only to the crystallized regions. It is generally agreed that water is a carrier for the NaOH throughout the structure and is responsible for a major part of the total swelling of the system, and that the range of constant composition begins at the concentration of caustic producing maximum swelling. As the concentration is increased above this point, the swelling and the amount of water adsorbed decrease rapidly even though sorbed caustic increases slightly. These swelling and sorbed water changes arise principally from the intercrystalline regions and would not affect the x-ray diagram. Thus, stabilization of a given composition may occur in the intercrystalline regions as a result of a change in the NaOH–H_2O interactions which minimize further addition of caustic by restriction of the carrier.

Before considering the lack of changes in the crystalline portion over this range, it seems necessary to emphasize the fact that, as previously discussed, the presence of a given x-ray diagram indicates only a constant molecular packing and does not define a chemical composition. Therefore the actual cellulose–NaOH ratio present in the crystalline regions may change over certain ranges without affecting the equilibrium packing appreciably. The swelling of the crystalline regions for any condition must be assumed to occur when the concentration of NaOH in the surrounding swollen intercrystalline gel exceeds a certain critical value. This value may be reached before any true equilibrium is reached and so long as this concentration at the instant of formation does not exceed certain limits, the swollen crystalline regions will assume a given configuration independent of small composition variations. Although the energy required to separate cellulose molecules in this swollen lattice is much lower than that in the original cellulose, this new lattice, once formed, still has large cohesive forces and will tend to retard further change in composition with varying concentration in much the same manner but to a lesser degree than the original cellulose lattice. Furthermore, if more sodium and hydroxyl ions are added, each additional pair will not cause any drastic change in packing. The alkali cellulose I crystal will not lose its identity until its composition is altered to the point that some other crystal form becomes more stable or the structure is lost completely by solution. Such a change occurs gradually in a range around 20% NaOH with formation of the so-called alkali cellulose II.

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[230] W. Vieweg, *Ber.*, **40**, 3876 (1907); **41**, 3269 (1908); **57B**, 1917 (1924).

Although a considerable tendency may be expected for flattening of a curve relating bath composition to composition of the cellulose phase as compositions approach those predicted for stoichiometric compounds, consideration of the complex polyphase structure of cellulose and the complex equilibria involved in cellulose–water–swelling reagent interaction leads to the conclusion that such stoichiometry is improbable as a general basis for swelling compound structure. The apparent stoichiometric compositions found by some investigators are partially coincidental results of simultaneous variations in packing, swelling, and variable composition in low-order and highly ordered structures. Reasoning similar to the above may be applied to observed variations in swelling compound structure and composition with temperature in aqueous media, or with temperature and pressure in anhydrous media. Variations in packing have been observed with temperature or pressure on swelling in liquid ammonia[33,34] and in anhydrous amines.[218] The swelling in anhydrous amines seems to decrease continuously with increasing temperature or decreasing pressure as would be expected from highly swollen structures formed through a physical adsorption process. It is the authors' opinion that the mechanism of addition complex formation by physical sorption is to be preferred for swelling compounds and that this mechanism is more generally applicable to problems encountered in commercial practice.

(d) **Effects of Intracrystalline Swelling on Structure.** The effect of intracrystalline swelling and deswelling cycles on the order–disorder structure of cellulose fibers is dependent upon the original unswollen structure and upon the nature of the swelling reagent. As previously discussed, the treatment of native cellulose fibers with mercerizing strength NaOH causes a decrease in the absolute crystallinity or lateral order and a decrease in both crystallite length and width as measured by either physical or chemical methods. Segal, Nelson, and Conrad[231] observed a similar decrease in crystallinity of cotton on treatment with quaternary ammonium hydroxides (e.g., Triton B) and anhydrous amines, and the effect may be regarded as general for natural cellulose fibers and swelling reagents containing only one active hydrogen-bonding group.

The effect of swelling and deswelling of regenerated cellulose structures with NaOH is usually just the opposite of that observed for native celluloses, that is, both the crystallinity and crystal size are greater after the swelling cycle.[129,155] Apparently very high local strains, produced by the rapid precipitation of regenerated cellulose in spinning baths, readjust to a more stable ordered configuration as the chain mobility is increased by swelling. The increase in crystallinity probably merely reflects the crystal growth at the expense of low-order regions in much the same manner as does the recrystallization on relief of strain by chain cleavage in hydrolytic media. The magnitude of the change varies from fiber to fiber. As expected, highly crystalline fibers such as Fortisan are only slightly affected, but the low-order, high-tenacity rayons show marked increases in order.

Swelling reagents such as the diamines, which are bifunctional and capable of forming "cross-links" between adjacent cellulose chains, show similar effects to a much lower degree. Native cellulose fibers show only slight decreases in crystallinity, and regenerated fibers show only slight increases in crystallinity after swelling in aqueous ethylenediamine.[232] The bifunctional amine "cross-links" apparently prevent rearrangement by forming a weak three-dimensional polymer network.

When a cellulose fiber is swollen, especially in an intracrystalline manner, the tendency is to produce a more random orientation, but the effect is not general for all swelling reagents. When either well-oriented natural cellulose or regenerated cellulose fibers are swollen in aqueous NaOH without external tension, a considerable shrinkage in the fiber direction occurs as the crystallite orientation decreases. This effect does not become pronounced in swelling mixtures below the concentration necessary for intracrystalline swelling. Swelling in anhydrous amines, however, has been reported to produce no significant decrease in the spiral orientation of cotton.[233] In any event, the original orientation can be maintained by holding the fiber at constant length during swelling or can be increased by stretching the swollen fiber.

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[231] L. Segal, M. L. Nelson, and C. M. Conrad, *J. Phys. & Colloid Chem.*, **55**, 325 (1951).

[232] J. A. Howsmon, unpublished results.

[233] L. Segal, M. L. Nelson, and C. M Conrad, *Textile Research J.*, **23**, 428 (1953).

(5) *Swelling of Cellulose Derivatives*

As a general rule, solvents for cellulose derivatives act first as a swelling reagent and then as a dispersing reagent. As with cellulose fibers, the swelling phenomena may be divided into those occurring as intercrystalline and those occurring as intracrystalline. In addition, a third type of swelling, designated as osmotically conditioned swelling, has been described.[234] In general, the behavior of cellulose derivatives on swelling is quite analogous to that of cellulose fibers.

Intracrystalline swelling is characteristic of most cellulose esters and ethers in suitable solvents and, as in cellulose, is usually preceded by intercrystalline swelling. For example, both cellulose triacetate and secondary cellulose acetates, when treated with acetone vapor or liquid, show both an increase in amorphous x-ray scattering characteristic of intercrystalline swelling and an increase in the lateral interchain distances characteristic of intracrystalline swelling. Cyclohexanone, methanol, benzene, pyridine, and chloroform–methanol mixtures all swell cellulose triacetate and produce an expansion of the crystal lattice at right angles to the fiber axis. Cellulose trinitrate is also capable of forming "swelling compounds" with a number of organic solvents without losing its fiber structure. Examples are the so-called cellulose "compounds" with cyclohexanone, acetone, fenchone and *m*-xylene.[235] Several "swelling compounds" formed between nitrocellulose and camphor have also been described.[236] These compounds are formed by the action of camphor in a solvent such as methanol or acetone. The type of compound formed seems to be influenced by both the concentration of camphor and the nature of the solvent. These phenomena are therefore quite analogous to swelling compounds of cellulose, and the general principles of compound formation previously discussed should apply.

Osmotically conditioned swelling[234] has been described as a process in which a swelling compound dissolves in the interior of a crystallite but is prevented by some semipermeable sheath from free diffusion into the mass of the liquid. It is marked by the retention of solid structure, the disappearance of an x-ray diagram characteristic of crystalline material, and the appearance of a liquid-type diagram. Although relatively little work has been done to elucidate this phenomenon, osmotically conditioned swelling could possibly represent a partially soluble stage preceding complete solution, a highly swollen stage in a borderline solvent corresponding to a melt, or a partially soluble stage resulting from incompletely reacted cellulose structures which are not swollen in the solvent.

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[234] W. A. Sisson, *Ind. Eng. Chem.*, **30**, 530 (1938)

[235] C. Trogus, T. Tomonari, and K. Hess, *Z. physik. Chem.*, **B16**, 351 (1932); **B17**, 241 (1932).

[236] K. Hess, T. Tomonari, and C. Trogus, *Z. physik. Chem.*, **B16**, 374 (1932).

(b) CELLULOSE DERIVATIVE FORMATION

The literature concerning the role of structure and the changes in structure during reaction in determining the reaction mechanism and nature of the reaction product is extensive and cannot be completely reviewed here. However, most of the data have been obtained from x-ray and microscopic studies of reacted materials with subsequent evaluation of the physical and chemical properties of the reaction products. No attempt will be made to discuss as separate classes the various types of reaction such as esterification and etherification, for insofar as structural principles are concerned all these reactions can be considered essentially similar processes subject to the general considerations given. The physical and chemical properties of the derivatives are discussed in greater detail in the various sections of Chapter IX so that only general reference will be made to them.

It is difficult to classify satisfactorily all the structural effects paralleling derivative formation, but it is often possible, as in the typical case of acetylation, to distinguish by x-ray diagram three more or less overlapping phases[234] consisting of: (1) the unchanged diagram of cellulose; (2) the diagram of the reaction product superimposed on the cellulose diagram; and (3) the diagram of the reaction product alone. According to Hess and Trogus,[237] the first of these phases is prevalent when the degree of substitution (D.S.) is below 1.3–1.7, the second for a D.S. range of 1.3–1.7 to 2.6, and the third when the D.S. is above 2.6. In nitration, however, the second phase does not consist of two superimposed diagrams but of an x-ray diagram of disordered or amorphous material. This type of diagram is usually found in nitrated samples containing from 7.5 to 10.3% nitrogen. Below 7.5% nitrogen, the nitrocellulose gives an x-ray diagram of cellulose usually as cellulose II; for nitrogen contents above 12.8%, a definite trinitrate x-ray diagram is obtained.[238] Unlike cellulose acetates the nitrocelluloses of different nitrogen content were prepared at equilibrium by variation in the nitrating mixture.

At one time, such data as these were thought to indicate that all the lower derivatives were mixtures of cellulose and its trisubstitution product. Therefore, the most likely reaction type was described as micellar heterogeneous, in which the reagent was assumed to penetrate the fiber, attack the surface of a crystallite, and convert it into the trisubstituted product. The reagent then proceeded inward, producing a partially reacted volume between the unreacted interior and the completely reacted surface. The three types of x-ray diagram described above would then correspond to (1) the unreacted interior, (2) the partially reacted area, and (3) the completely reacted surface, and the over-all types would change as the reaction proceeded. However, other reaction models were presented and it is now generally agreed that no single model will adequately explain all reactions. This view was aptly stated by Lorand and Georgi[239] in 1937: "There is evidence to support the view that cellulose reactions do not follow a single pattern, and that the type varies, depending on the reaction partner, its concentration, the reaction medium, temperature, etc. It is quite probable that all the reaction models, such as surface reactions, topochemical heterogeneous reactions, permutoid or quasihomogeneous reactions as well as the previously mentioned micellar heterogeneous reactions may apply to cellulose in one case or another, depending on circumstances."

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[237] K. Hess and C. Trogus, *Z. physik. Chem.*, **B15**, 157 (1932).

[238] F. D. Miles and J. Craik, *J. Phys. Chem.*, **34**, 2607 (1930).

Almost all cellulose reactions start with fibrous cellulose which is, as previously discussed, usually partly crystalline and partially noncrystalline. Most reactions are therefore heterogeneous to some extent. The nature and extent of heterogeneity in any given case is closely associated with the extent of swelling of the cellulose structure in the reaction medium, the rate and extent of diffusion of reactants into the structure, the reaction velocity, and the behavior of the reaction product in the medium. The products of the heterogeneous reaction in various cases will usually be nonuniform in one or more of the following respects: (1) the surface of the fiber will have reacted more than the interior; (2) the low-order noncrystalline regions will be substituted to a greater extent than the crystalline regions; (3) even though the substituents may react randomly along the molecule, the degree of substitution of an individual anhydroglucose unit may vary randomly from zero to three.

Though complete discussion of all possibilities is impossible, the general basis for the above concepts can be readily illustrated by examples with particular emphasis on the overwhelming importance of swelling in rendering the order–disorder structure available for reaction and in determining the course of the reaction. If a dry unswollen cellulose is treated with a reactant in a solvent which has no tendency to penetrate and swell the cellulose or the reaction product, the reaction will in general be confined to the fiber surface. A similar tendency is also found on treating swollen celluloses with reagents of such large molecular volume that diffusion within the swollen structure is impossible. The reactions of cellulose with diazomethane in ethyl ether[119] and with thallous ethylate in certain ethers and hydrocarbons[115] are essentially reactions of the first type, whereas the alkylation of alkali celluloses or trisodium cellulose in anhydrous solvents is most probably of the second type.[113] These reactions are not critically dependent on the cellulose structure itself. Other reactions which have been called macroheterogeneous or topochemical are characterized by the fact that the reaction starts on the fiber surface and proceeds inward from layer to layer so that at a given time during the reaction the extent of reaction will be greatest on the outside of fiber and least in the core. These reactions may occur under a variety of conditions. They are most commonly associated however with conditions in which either (1) the reactant itself or a solvent carrier possesses limited swelling power and diffuses into the cellulose very slowly or (2) the reactant or solvent carrier may penetrate the cellulose but the reaction product formed is not swollen by either reactant or solvent. These reactions are principally dependent on diffusion conditions and the relative rates of reaction and diffusion. If the reaction rate becomes much greater than the diffusion rate, the reaction may be confined to the fiber surface. Typical macroheterogeneous reactions are the acetylation of unswollen cellulose with acetic anhydride in indifferent solvents such as toluene or benzene,[240–242] the benzylation of alkali cellulose,[239] and the de-esterification of cellulose acetates and nitrates in nonswelling solvents.

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[239] E. J. Lorand and E. A. Georgi, *J. Am. Chem. Soc.*, **59**, 1166 (1937).

If the cellulose is swollen either by the reactant, by the solvent, or by preswelling with a third component which may subsequently be replaced, the reactions invariably become microheterogeneous in nature and their course depends on the cellulose structure. In the literature, these reactions have principally been classified as one of two types, (1) micellar heterogeneous or (2) permutoid. Though the literature on these types is quite extensive and each type has been variously stated to be the most probable for most cellulose reactions, no general agreement has been reached. Present knowledge indicates that the difference between these types is one of degree and, therefore, that there is little basis for argument that either

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[240] K. Kanamaru, *Helv. Chim. Acta*, **17**, 1429 (1934).

[241] E. Elöd, H. Schmid-Bielenberg, and L. Thoria, *Angew. Chem.*, **47**, 465 (1934).

[242] E. Elöd and H. G. Frohlich, *Textile Research J.*, **18**, 487 (1948).

mechanism is most probable for all cases. A reconciliation of the various mechanisms can be made by the following widely accepted views.

In general, swelling acts to loosen the order–disorder structure of cellulose and make it more accessible for reaction. If the swelling is intermicellar, only the low-order regions are swollen, and because of imbibition of the swelling liquid, the penetration of reagents into these regions and subsequent reaction become quite rapid. Any crystalline region is less available for reaction and will react at a slower rate either at the lateral surface or at the fringed ends. This type of reaction corresponds to the modern view of a micellar heterogeneous reaction. If the swelling is intramicellar, diffusion into the crystalline regions may be aided by the expansion of the crystal lattice, but again the diffusion rate and hence the reaction rate lags behind that in the low-order regions. For example, Timell[243] has reported that the reaction of cellulose swollen in liquid ammonia, which forms a swelling compound in the crystalline regions, exhibits a two-stage conversion rate quite similar to that observed in aqueous hydrolysis of cellulose. This implies a very slow rate of reaction even in highly swollen crystalline regions. Thus, all cellulose reactions except those carried out in solution are heterogeneous in nature. Therefore most questions concerning reaction mechanisms concern the possibility that in a given case the crystalline regions can react to the same extent as the amorphous regions to give a uniform reaction product. This is possible if any one of three conditions is fulfilled: (1) the reaction goes to completion; (2) the fiber goes into solution during reaction and all structural effects are lost; or (3) an equilibrium is attained in which the extent of reaction is determined by the reagent concentration. The first and second of these conditions are used in the preparation of uniform organic esters of D.S. less than 3 in that a uniform completely substituted product is partially hydrolyzed in solution to the desired substitution. These conditions are necessary in all reactions which are extremely heterogeneous in nature, such as formylation and acetylation. The third condition applies to nitration, during which an equilibrium is attained. The nitration of cellulose most closely fits the permutoid mechanism which demands that each cellulose chain has the same probability of reacting. This most probably arises because the reagent itself, nitric acid, forms a swelling compound with cellulose and attains fairly high concentrations in the crystalline regions. Therefore, the crystalline regions react rapidly and a fairly uniform reaction throughout the sample results. In other cases the crystallite swelling reagent, such as sodium hydroxide or liquid ammonia, is merely a carrier for a reactant such as metallic sodium, and, in general, a less uniform reaction occurs. Thus, the delineation of cellulose reactions into classes such as micellar heterogeneous and permutoid seems too perfect. There is no distinct line between the two classes but rather there are gradual transitions from more heterogeneous reactions to less heterogeneous reactions as intercrystalline and intracrystalline swelling increase. The most homogeneous reactions occur under special conditions such as those in nitration in which the reactant itself diffuses rapidly into even the highly crystalline structural elements. The low-order or amorphous portions of the fiber will react in a permutoid manner in all cases involving penetration of the reagent into swollen celluloses.

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[243] T. Timell, *Svensk Kem. Tid.*, 61, 125 (1949).

(c) CRYSTALLINE STRUCTURE OF CELLULOSE DERIVATIVES

Because of the lack of single crystals and often of fiber diagrams, little definite information is available regarding the unit cell structures of cellulose derivatives even though the literature on these structures is extensive. Complete values have been published for cellulose triacetate,[244] cellulose trinitrate,[244–246] methyl celluloses,[247] and dinitrocelluloses.[245,246] In most cases polymorphic forms such as methyl celluloses I and II and cellulose triacetates I and II have been proposed but no general agreement has been attained on either the unit cell structures[246] or the existence of polymorphic forms,[47] and no thorough survey of various possibilities has been made. It is the authors' opinion that much of this published work on both unit cell structure and polymorphism should be reconsidered before definite conclusions are drawn, inasmuch as the bulk of the work was done before the complexity of the application of x-ray diffraction was fully understood and before the concept of lateral order and lateral-order distribution was accepted.

Baker[47] has most clearly stated this case as follows: "Apparent variations in the equatorial spacings, accompanied always by changes in the sharpness of the spots (in x-ray diagrams), have led to the vast literature[234] on different forms of cellulose derivatives. Present knowledge makes it probable that the numerous forms of cellulose esters, ethers, etc., reported really represent different states of local order. Thus, they are not actual polymorphic forms stable over certain temperature ranges or conditions of preparation." Baker also points out that differences in x-ray diagrams of different forms are not so striking as in the case of cellulose I and II but that the emphasis is on the differences in sharpness and intensity of the diffraction spots rather than on their arrangement and that exactly such differences will occur from variations in lateral order induced by heat, solvents, plasticizers, or variations in chemical composition.[47,248]

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[244] R. O. Herzog, *J. Phys. Chem.*, **30**, 457 (1926); *Helv. Chim. Acta*, **9**, 631 (1926).

[245] M. Mathieu, *Compt. rend.*, **198**, 1434 (1934); **199**, 55 (1934); **200**, 143 (1935).

[246] F. Happey, *J. Textile Inst.*, **41**, T381 (1950).

[247] C. Trogus and K. Hess, *Z. physik. Chem.*, **B4**, 321 (1929).

According to this view, cellulose triacetate I, which exhibits relatively large equatorial spacings characteristic of lateral disorder, would be considered a metastable, disordered state, whereas cellulose triacetate II would represent a similar structure of a higher lateral order of crystallinity. This view agrees with the observations that certain swelling agents increase the lateral interchain distances in form I but do not change these distances in form II. The disordered form I, having elements of liquid structure, could be continuously changed by swelling whereas the ordered form II would exhibit no such reversible swelling phenomena since the chains are precisely arranged. Other recent workers[246] have concluded, however, that on fibrous acetylation the triacetate is first produced as form I and then transformed to form II at higher temperatures. In this view triacetate I would be analogous to cellulose I and triacetate II to cellulose II. In any event the cellulose triacetate II form seems to be the normal modification for this is the form precipitated from solution or prepared by intracrystalline swelling of cellulose triacetate I.

The exact arrangement of substituted groups is largely a matter of assumption, but in all cases the chains in the derivative can be arranged parallel to one another at well-defined distances which increase with the completeness of substitution and with increasing length of the substituent. It is probable that for the most part the substituent groups are essentially normal to the length of the cellulose molecule and lie in the plane of the anhydroglucose unit. The identity period along the molecule of most cellulose derivatives is 10.3 A. as in celluloses I and II, corresponding to the length of two anhydroglucose units, but may vary as a multiple of 5.15 A., the length of one anhydroglucose unit. The two most common periods other than 10.3 A. are 15.4 A. and 25.6 A.

Although the crystal structure of a cellulose derivative is frequently associated with a definite chemical composition such as cellulose triacetate or dinitrocellulose, the actual crystal structure may remain constant over wide ranges of chemical composition. Thus, the lattice structure of crystalline secondary cellulose acetate (D.S. = 2.5) is identical to that found in

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[248] C. S. Fuller, W. O. Baker, and N. R. Pape, *J. Am. Chem. Soc.*, 62, 3275 (1940); 64, 776 (1942); 65, 1120 (1943).

crystalline cellulose triacetate II. The unsubstituted hydroxyl groups apparently crystallize isomorphically in the cellulose triacetate II lattice.[246] Similarly, for cellulose acetates of low D.S. the preferred packing form would be like that of cellulose II, whereas at intermediate ranges of substitution over which the packing tendencies of hydroxyl and acetyl groups are in direct competition, the preferred crystal form is most probably a highly disordered form and may be unlike that of either cellulose II or cellulose triacetate II. Over this intermediate range the actual packing observed is probably critically dependent on the method of preparation.

Isomorphic replacements of this type may occur in many other partial derivatives. Happey[246] has explained the x-ray diagrams of nitrocelluloses of different nitrogen content on the basis of isomorphic replacement of hydroxyl groups in the crystal lattices of dinitro- and trinitrocellulose. It is the authors' opinion that there is reasonable doubt that the crystal lattice described for dinitrocellulose[245,246] is either a true polymorphic form or characteristic of dinitrocelluloses other than those prepared by normal fibrous nitration procedures. The possibility that dinitrocelluloses would not crystallize in the same crystal lattice after solution, reprecipitation, and recrystallization has not been thoroughly investigated. In any event, many uncertainties still exist in the lattice structure of cellulose derivatives, and a great deal of study, preferably with samples of maximum order prepared by optimum crystallization procedures for each chemical composition, will be required before general conclusions can be made.

(d) CRYSTALLINITY AND LATERAL ORDER IN CELLULOSE DERIVATIVES

The concepts of coexisting ordered and disordered states of various degrees of order and disorder as discussed previously for cellulose appear to be generally applicable to solid polymers and can be taken directly as expressing the possible variations in fine structure of cellulose derivatives. The problem is more complex, however, for the ultimate or highest state of order possible in a cellulose derivative varies with the type of derivative and with the chemical composition of partially substituted or mixed derivatives. For cellulose triesters, only lateral disorder of molecules of uniform composition, as previously discussed for cellulose, need be considered. For cellulose partial esters or mixed esters, however, steric effects from variation in size or chemical nature of the substituent groups may lead to permanent or semipermanent disorder[248] which may in some cases extend into the crystallized regions. Even though a secondary cellulose acetate and the primary cellulose triacetate may be crystallized in the same crystal form to the same extent so that the crystallinity may be considered constant as far as mechanical properties are concerned, it is difficult to establish this essential structural equivalence because of the dependence of experimental methods, such as x-ray diffraction or chemical reactivity, on chemical composition. Thus, because of the limitation of experimental methods in distinguishing between various types of disorder and chemical composition effects, the expression of the fine structure of cellulose derivatives is still essentially qualitative.

Timell[114] determined the relative accessibility of three allyl celluloses prepared from cotton linters, a sulfite wood pulp, and a viscose rayon by evaluation of the reaction of the derivative with iodine bromide. He found that the amount of accessible material in each sample apparently remained unchanged throughout the etherification. At least the accessibility of each of the three derivatives was of the same order of magnitude as the accessibility of the original mercerized samples to periodic acid. The fact that those parts of the structure that were ordered in the alkali cellulose remain so in a completely substituted derivative is a previously unreported observation. This effect is probably limited to cases in which the fiber structure is retained throughout the reaction.

Most structural studies on cellulose derivatives have utilized x-ray diffraction methods and usually involve a direct comparison of the x-ray diagram of a given sample with that of a sample of the same composition in a standard or limiting state of local order or orientation.[47] These methods are based on the variation of the position, intensity, and number of interferences in the x-ray diagram with the perfection of molecular packing. In general, the lateral distance between molecules becomes smaller and the x-ray interferences become sharper and increase in number with increasing lateral order, so that if a crystallized sample is used as reference, the lateral order may be related to the appearance, position, and intensity of a given feature in the diagram.

Although the crystallinity of cellulose fibers is little affected by heat after crystallization has once taken place, most trisubstituted cellulose derivatives may be solidified from the molten state to produce either a crystalline or amorphous structure depending upon the temperature gradient.[248] Thus, if cellulose triesters are solidified from their melts at a temperature a few degrees below the melting point, highly crystalline solids are produced. If they are quenched at temperatures of at least 200°C. below the melting point, the disordered array of the liquid is preserved. Quenching in this manner does not leave the molecules disordered in the same sense that a liquid is amorphous. Instead it apparently leaves chain sections locally parallel but randomly rotated around their long axis, for if these materials are subsequently annealed at a temperature below the melting point, the molecules acquire sufficient kinetic energy to rearrange into a stable crystalline configuration.[248] These effects are illustrated by the x-ray diagrams in Figure 30. The extent of the crystallization in any given case can be controlled by control of the time and temperature of annealing. Thus, low or intermediate crystallization can be produced by annealing for shorter times or at lower temperatures than those which produce high crystallinity.

The action of heat in rearranging the amorphous structure of quenched cellulose esters indicates a high degree of mobility in the solid state of chain segments which are internally plasticized by ester groups. As expected, the crystallization can be accomplished more easily and usually with better control in esters that are essentially completely substituted with a single kind of substituent than in many of the partial or mixed esters encountered commercially. In these latter cases semipermanent disorder is stabilized either by the superposition of hydrogen bond formation on the internal plasticization by ester groups in partial esters or by the difference in length of the substituent groups in mixed triesters. In either case the inherent tendency to crystallize is limited. Thus, cellulose acetate rayon in which the D.S. is about 2.5 usually exhibits low crystalline order, and no practical method of controlling the order in various products as in the case of viscose rayon is known.[249] Similarly, crystalline order in cellulose acetate butyrate is dependent upon both the total substitution and upon its distribution between acetyl and butyryl groups.[47] Only the esters essentially completely substituted yield ordered x-ray diagrams, but even so, permanent disorder occurs in completely substituted esters which contain roughly equal amounts of acetyl and butyryl groups. Local disordering by chemical composition as in the above cases resembles closely the disorder resulting from quenching but differs in that annealing by heat-treatment does not restore order. Many of the compatible plasticizers used in cellulose derivatives also cause permanent disordering of this type apparently by association of the plasticizer with specific groups of the polymer and subsequent weakening of the interchain forces. In these cases the plasticizer is not concentrated in the amorphous regions but gradually disorders the whole structure.[47]

Crystallization from disordered states arising from either quenching or chemical composition can be greatly facilitated by the use of solvent or swelling agents. Spence,[250] using x-ray and birefringence methods on cellulose triacetate films, noted that "good" solvents such as ethylene chlorohydrin give films of higher crystallinity than "poor" solvents such as chloroform. Similarly, Fuller, Baker, and Pape[248] noted that the extent of crystallization occurring on exposure of quenched esters to solvent vapors at 25°C. was dependent on the nature of the solvent and could be related directly to the properties of the films formed. Thus chloroform is a "better" solvent for cellulose tributyrate than acetone; acetone films of tributyrate are less crystalline than those from chloroform. These concepts are apparently generally applicable. For example, Mathieu's observa-

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[249] R. W. Work, *Textile Research J.*, 19, 381 (1949).

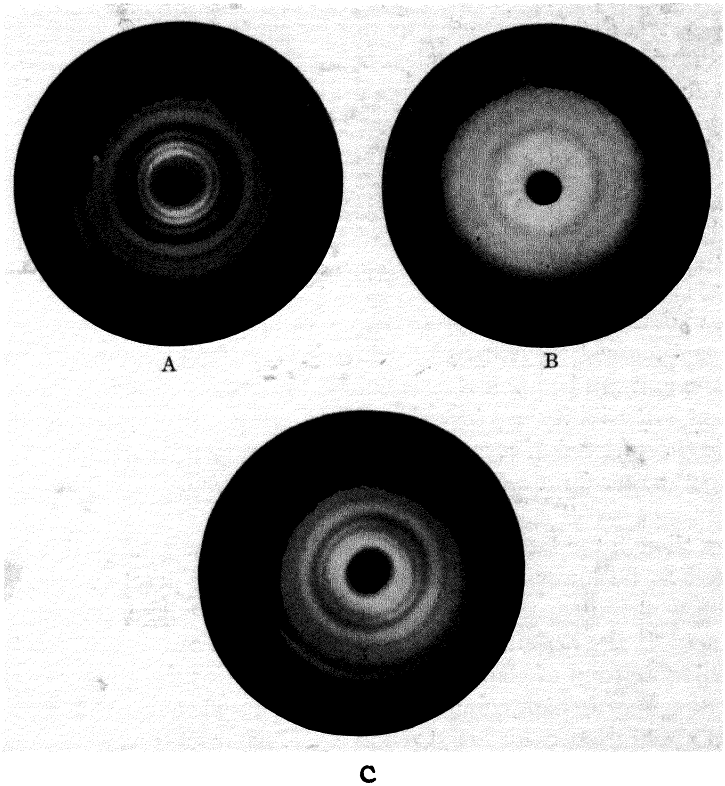

Fig. 30. X-ray diagrams of cellulose triacetate showing effect of heat-treatment (Fuller, Baker, and Pape[248]). (A) Solidified near melting point (which is about 240° C.); (B) quenched at −75° C.; (C) is (B) annealed for 2 hrs. at 225° C.

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[250] J. Spence, *J. Phys. Chem.*, **45**, 401 (1941).

tion[251] in x-ray diagrams that films of nitrocellulose dried at 70°C. were more crystalline than those dried at 20°C. indicates the ease of extension of these concepts to cellulose nitrate.

In cases of semipermanent disorder in partial or mixed esters, solvent action or heating supplemented by swelling action may cause crystallization when heat alone will not. A mixed partial cellulose acetate butyrate can be crystallized by acetone vapor or by water at 100°C. even though no crystallization results from dry heat below the softening point. The secondary cellulose acetates of commerce are generally not very crystalline and cannot be readily crystallized by heat below the softening point. However, crystallization occurs readily at temperatures of the order of 100° to 150°C. in the presence of limited swelling reagents such as diacetone alcohol,[252] 5% dioxane in water,[246] methanol,[253,254] or water vapor.

(1) *Relationship of Crystallinity to Physical Properties*

The variation of physical properties with changing crystallinity or lateral order as discussed previously for cellulose is generally applicable for linear polymers and can be applied to cellulose derivatives as well. Thus, toughness and extensibility are favored by high order. In general, greater difficulty is encountered in correlating a physical property with a single lateral-order parameter for a cellulose derivative than is normally found for cellulose.

Even though the lateral order as measured by x-ray diffraction would be expected to be lower for crystalline secondary cellulose acetate than for crystalline primary cellulose triacetate, the crystalline regions in both cases may fit the definition of a crystal when defined as any unit volume containing a group of chains arranged in space in such a manner that the cohesive energy is high enough that this group of chains will behave as a unit on application of an external force. Thus, insofar as a physical property such as elongation or tenacity is concerned, the crystallinity may be identical and there would be no regular variation of the physical property with this internal disorder of crystallites at normal temperature. In other words, crystalline regions of equivalent size and shape may react identically to stress even though the degree of crystalline perfection is different.

Similarly, films of crystalline cellulose esters are more brittle when cast from polar solvents and there seems little doubt that the increased brittle-

[251] M. Mathieu, *Trans. Faraday Soc.*, **29**, 122 (1933).

[252] E. Freund and F. Deutsch, *Rayon Textile Monthly*, **21**, 280 (1940)

[253] D. Vermaas, P. H. Hermans, and A. Weidinger, *J. Polymer Sci.*, **2**, 406 (1947).

[254] G. Centola, *Atti accad. Lincei*, **23**, 881 (1936); *Chem. Abstracts*, **31**, 2417 (1937).

ness is related to higher crystallinity of films cast from good solvents. In other cases of greater commercial importance, such as ethyl cellulose or cellulose acetate plastics, wide variations in flexibility can be produced with little or no change in crystallinity or lateral order. These variations are a function of sheet structure which is determined by the solvent power of the solvent for the polymer in question.[255,256] Fuller discussion of these phenomena will be found in Chapter X-A.

(e) ORIENTATION IN CELLULOSE DERIVATIVES

The familiar uniaxial fiber structure was noted in cellulose triacetate as early as 1924.[257] Moreover, in cellulose derivatives generally, it is possible to produce all the classes of orientation found in native and regenerated celluloses, and the same terminology applies. The occurrence of orientation in cellulose derivatives is most analogous to the formation of orientation in regenerated cellulose fibers or films upon dehydration of the swollen gel, as outlined previously with the added possibility that the original unoriented state may be either swollen as in cellulose or a melt as in the thermoplastic derivatives. The formation of spontaneous orientation occurring during cooling a molten derivative or mechanically deforming a heat-softened derivative is quite similar to the behavior of cellulose on dehydration, and the two cases can at least in a general way be treated as identical phenomena. The principal difference lies not in the type or degree of orientation produced but in the fact that greater changes in crystallinity may occur in cellulose derivatives as a result of the deformation necessary to produce orientation than are normally found in regenerated cellulose in which fairly great orientation differences can be produced with little or no change in crystallinity.

Because of the nature of dry-spinning operations, the cellulose acetate rayons of commerce are only slightly crystalline and possess a slight degree of preferred orientation in the direction of the fiber axis. The orientation may be increased slightly by dry-stretching or more readily and completely by stretching at high temperature, by stretching in a swelling reagent, or by using a combination of swelling and high temperature.[249] Thus, the orientation in cellulose acetate filaments can be changed progressively by placing the yarn in a swelling reagent such as a mixture of dioxane and water,[258] stretching the yarn in the swollen condition, and then removing the

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[255] H. M. Spurlin, A. F. Martin, and H. G. Tennent, *J. Polymer Sci.*, **1**, 63 (1946).

[256] H. C. Haas, L. Farney, and C. Valle, Jr., *J. Colloid Sci.*, **7**, 584 (1952).

[257] R O. Herzog and G. Londberg, *Ber.*, **57**, 329, 750 (1924).

[258] H. Dreyfus, U.S. Patent 2,053,766 (Sept. 8, 1936); *Chem. Abstracts*, **30**, 7342 (1936).

swelling reagent by washing or evaporation. The orientation so produced is uniaxial, and as a general rule no marked increase in crystallinity is observed with increasing orientation. Regenerated cellulose yarns marked by very high tensile strength, such as Fortisan, are produced by saponification of these highly oriented cellulose acetate yarns.

Sheets or films of cellulose esters which are cast from solvents,[259] rolled to half their initial thickness and compression-molded at low temperatures or injection-molded under suitable conditions,[47] usually exhibit a uniplanar orientation in which the long axes of the crystal nuclei are parallel to but randomly distributed within the plane of the sheet. In actual practice, the relative severity of the pressing or molding also causes some preferred orientation of the (101) planes of the crystallites parallel to the plane of the sheet so that some degree of selective uniplanar orientation occurs.

Biaxial orientation can be formed in cellulose esters by rolling a fiber or strip which has been previously oriented uniaxially by drawing.[47] These plastic deformation processes producing biaxial orientation usually cause considerable disruption of the original crystalline order quite similar to that observed on grinding of dry cellulose.[54,55] As expected, the system can be reordered by annealing at elevated temperatures, but the upper limit for annealing by temperature or swelling reagents is lower for oriented than for unoriented polymers because eventually the orientation of the long-chain axes in respect to the sample surfaces is lost.

(1) *Relationship of Orientation to Physical Properties*

The expected variations in physical properties of cellulose esters with increasing orientation are essentially the same as those previously discussed for cellulose fibers. Thus in fibers the tenacity will increase and elongation will decrease with increasing uniaxial orientation, and in sheets or films the resistance to tearing increases with increasing uniplanar or selective uniplanar orientation.

Any interpretation of the physical properties of cellulose esters in terms of fine structure must be based on both crystalline order and orientation within a given sample. From the above discussion of the possible ranges of both these factors in cellulose esters, it is evident that the wide variety of properties occurring in various spun, cast, and molded objects arise, to a great extent, from structural variations dependent on chemical composition, mechanical stress during formation, and temperature and time effects in molding cycles.

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[259] J. G. McNally and S. E. Sheppard, *J. Phys. Chem.*, **34**, 165 (1930).

C. MICROSCOPIC STRUCTURE

CHARLES W. HOCK

The nature of the cellulose molecule determines the broad pattern of the chemical and physical behavior of cellulose. The properties of cellulose are, however, also very greatly influenced by the manner in which the molecules are arranged, both with respect to each other and also with regard to the larger units such as cells and fibers in which they lie. Despite the great amount of work done on elucidation of the organization of cellulose, there is as yet no completely satisfactory picture of it. Nevertheless, with the advent of new tools and techniques, noteworthy progress is being made.

In the foregoing section the contributions of x-ray diffraction studies toward an interpretation of the small-scale structure of cellulose were discussed. In the present section the structure of cellulose in the range of dimensions amenable to investigation by microscopical techniques will be considered.

Cellulose is the chief component of the walls of practically all plant cells, but technologically it is largely the fiber form which is utilized. Indeed, it is this very fiber structure which accounts for the usefulness of cellulose in many applications, as in the manufacture of textiles. On the other hand, because of its influence on the course of chemical reactions, fiber structure is sometimes a hindrance, as in the utilization of cellulose as a chemical raw material. For these reasons some discussion of fiber structure properly forms a part of any comprehensive treatise on cellulose.

The fiber structure of some of the more important sources of cellulose is discussed in the following pages. Although their specific structural patterns vary, all forms of cellulose show certain similarities which seem to be fundamental.

1. Native Cellulose

(a) LIGHT MICROSCOPICAL INVESTIGATION

(*1*) *Structure of Native Sources of Cellulose*

(a) **Seed Hairs.** Of the seed hairs which are used commercially, the cotton fiber is unquestionably the most important. Because of the great economic value of cotton, the attention of many investigators has been directed toward a study of this fiber, and consequently considerable information concerning its structure and behavior is available.[1]

Seed hairs are so named because they arise as cellular outgrowths of the seed coat. In cotton, incipient fiber formation is recognized by swelling of the outer wall (i.e., the exposed surface) of the epidermal cells of the cotton seed. By growth and elongation, these swellings form tubular outgrowths which, although only 15 to 20 microns in diameter, may reach a length of an inch or more. The long lint fibers originate on or about the day the cotton plant comes into flower: later, up to 10 days or more after flowering, other epidermal cells start to elongate, and these give rise to short fuzz fibers.[2–6] The long lint fibers, which are used primarily by the textile industry, are referred to in commerce as "cotton." The fuzz fibers and those broken lint fibers which remain after ginning constitute the "linters," which are used extensively as a source of chemical cellulose. (See Chapter VI-B on "Cotton Lint and Linters.") Elongation of the fiber-forming cells continues up to about 20 days after flowering, at which time growth in length ceases. The fibers have then reached their maximum length, the later-formed fuzz hairs never having achieved the length of the lint fibers, which originated at the time of flowering.

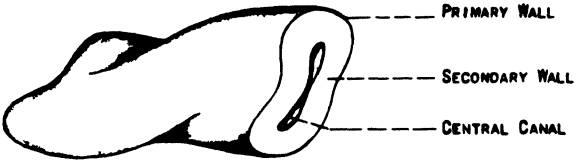

Fig. 31 Sketch showing gross structure of mature cotton fiber (according to Berkley[6]).

During the period of elongation the fibers possess only a thin *primary wall,* which encloses the protoplasm. After growth in length has ceased, the thickness of the fiber wall is greatly increased by deposition of the *secondary wall,* which is laid down on the inner surface of the primary wall, thereby decreasing the bore of the central canal or lumen. Increase in wall thickness then continues for several weeks, until the cotton boll opens and the fibers dry up and die. The structural relationships which prevail in a mature fiber are illustrated diagrammatically in Figure 31.

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[1] E. A. Flint, *Biol. Revs. Cambridge Phil. Soc*, **25,** 414 (1950).

[2] A. G. Lang, *J. Agr. Research,* **56,** 507 (1938).

[3] D. B. Anderson and T. Kerr, *Ind. Eng. Chem.,* **30,** 48 (1938).

[4] C. W. Hock, R. C. Ramsay, and M. Harris, *J. Research Natl. Bur. Standards,* **26,** 93 (1941); *Am. Dyestuff Reptr.,* **30,** 53 (1941); *Textile Research,* **11,** 200 (1941).

[5] C. W. Hock, *Textile Research J.,* **17,** 423 (1947).

[6] E. E. Berkley, *Textile Research J.,* **18,** 71 (1948).

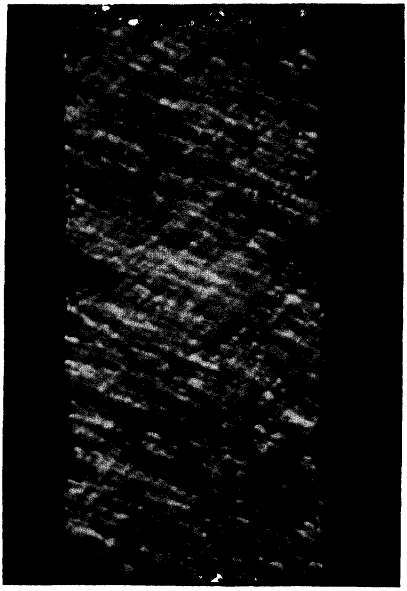

Fig. 32. Cellulose in the primary wall. An immature cotton fiber stained with Congo red and photographed between crossed nicols to show the apparent netlike arrangement of the cellulose. Magnification ×900.

The thin primary wall is only a few tenths of a micron thick and accounts for only about 5% of the weight of the fiber. It consists largely of waxy and pectic substances, plus a small amount of cellulose. As ordinarily observed with the light microscope it shows little or no evidence of internal structure. When the wall is stained with a dye such as Congo red and then examined with a polarizing microscope, the appearance of the fibers suggests a netlike arrangement of the cellulose[3,4,7–9] (Fig. 32). However, this interpretation has been questioned by Roelofsen,[10,11] who claims that the

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[7] W. L. Balls, *Proc. Roy. Soc.* (*London*), **B95**, 72 (1923).

[8] W. L. Balls, *Studies of Quality in Cotton*, Macmillan, London, 1928.

[9] T. Kerr, *Textile Research J.*, **16**, 249 (1946).

[10] P. A. Roelofsen, *Biochim. et Biophys. Acta*, **7**, 43 (1951).

[11] P. A. Roelofsen, *Acta Botanica Neerlandica*, **2**, 218 (1953).

striations are caused by wrinkles in the cell wall. The meager information obtained through light microscopical studies of the primary wall has recently been supplemented by electron microscopical studies, which will be discussed in a later section. Although the primary wall comprises only a small part of a mature cotton fiber, it nevertheless greatly influences dye-

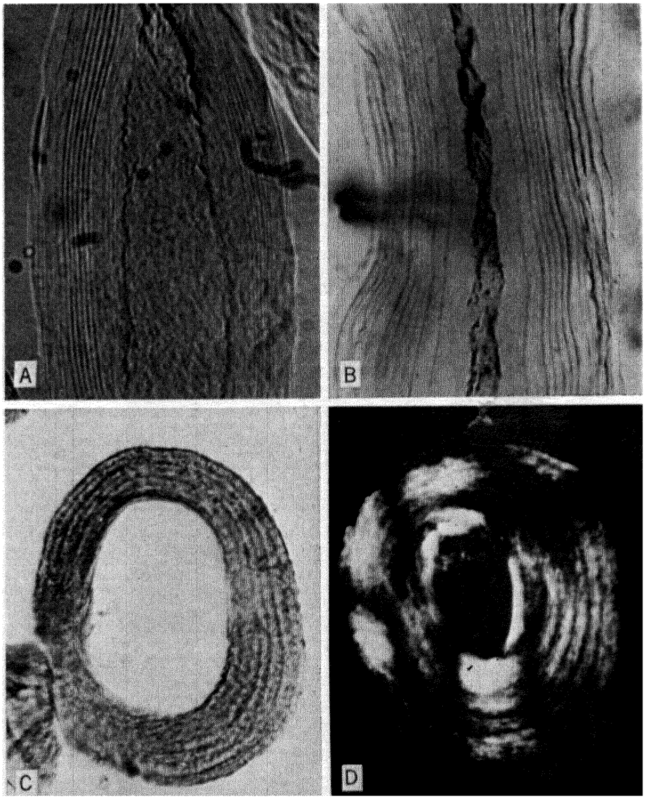

Fig. 33. Layered structure of the secondary wall of cotton. Fibers swollen in cuprammonium hydroxide solution: (A) Longitudinal view showing layered pattern caused by alternation of cellulosic layers differing in porosity and in density; magnification ×340. (B) Longitudinal view showing layered pattern caused by alternation of cellulosic and noncellulosic layers; magnification ×310. (C) Cross section; magnification ×615. (D) Cross section photographed between crossed nicol prisms. Magnification ×450.

ing, finishing, wettability, reactivity, attack by microorganisms, and other fiber properties.[12–16]

The principal chemical constituent of cotton, and the one chiefly responsible for its commercial usefulness, is cellulose. The secondary wall contains the bulk of the cellulose in a mature fiber. The gross structure is visible in unswollen fibers, but the detailed pattern is studied to better advantage in expanded material. Although it is recognized that swelling agents produce some distortion, this technique seems justifiable, inasmuch as corroborative evidence can be obtained indirectly from polarization and x-ray studies.

The examination of swollen fibers reveals a layered pattern in the secondary wall. In the longitudinal view these layers look like stripes running parallel to the long axis of the fiber (Fig. 33, A and B); in cross-sectional view they look like concentric circles (Fig. 33, C and D). In other words, the layers of which the secondary wall is composed resemble concentric tubes In most fibers this pattern is due to the alternation of layers of cellulose which differ in porosity and in density (Fig. 33A). In other fibers the layered configuration is due to the alternation of layers of cellulose with layers of noncellulosic material (Fig. 33B). In either case adjacent layers appear bright or dark as observed between crossed nicol prisms (Fig. 33D). The chemical nature of the noncellulosic layers has not been established, but their reactions are similar to those of the primary wall.[5] Noncellulosic layers are generally absent in the secondary wall of the long lint fibers, but such layers sometimes occur in the fuzz fibers. Studies of the growth of cotton fibers have demonstrated that two adjacent layers are laid down every 24 hours during the period of secondary-wall formation and that they constitute, therefore, a daily "growth ring."[4,17,18] The width of the rings, which ranges from 0.1 to 0.5 micron, appears to fluctuate with variations in the environmental conditions which prevail during growth.

The layers of cellulose are further subdivided into fine threadlike fibrils, each only a few tenths of a micron in diameter, oriented in a helix at an angle of 25° to 45° to the main fiber axis. The angle of orientation varies

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[12] R. Haller, Z. *Farben-Ind.*, 6, 125 (1907); *Chem. Zentr.*, **1907, II**, 953.

[13] A. M. Sookne and M. Harris, *J. Research Natl. Bur. Standards*, **26**, 65 (1941); *Am. Dyestuff Reptr.*, **30**, 29 (1941); *Textile Research* **11**, 307 (1941).

[14] C. F. Goldthwait, H. O. Smith, and M. P. Barnett, *Textile World*, **97**, 105 (1947).

[15] V. W. Tripp, A. T. Moore, and M. L. Rollins, *Textile Research J.*, **21**, 886 (1951).

[16] V. W. Tripp and M. L. Rollins, *Anal. Chem.*, **24**, 1721 (1952).

[17] W. L. Balls, *Proc. Roy. Soc.* (*London*), **B90**, 542 (1919).

[18] T. Kerr, *Protoplasma*, **27**, 229 (1937).

in different layers and changes many times from an S to a Z spiral,[19] and vice versa, at irregular intervals along the fiber axis. Frequently, although not invariably,[9] the fibrils in the outermost layer of the secondary wall (i.e., the winding[4,5,9]) are oriented in a direction which is opposite from the spiral of the fibrils which lie immediately beneath it. In other words, if the winding makes an S spiral, the fibrils beneath the winding make a Z spiral. Furthermore, the places where the fibrils in different layers reverse their direction of spiral often coincide. This condition accounts for the extinction bands which are observed when unswollen fibers are placed approximately parallel to the plane of vibration of the light passing through one of two crossed nicol prisms (Fig. 34A). The relatively high birefringence of the fibers as a whole is then interrupted by dark extinction bands which coincide with the points where the fibrils reverse their direction of orientation (Fig. 34B). These reversals are sometimes preferred locations of break when the fibers are ruptured in tension.[20]

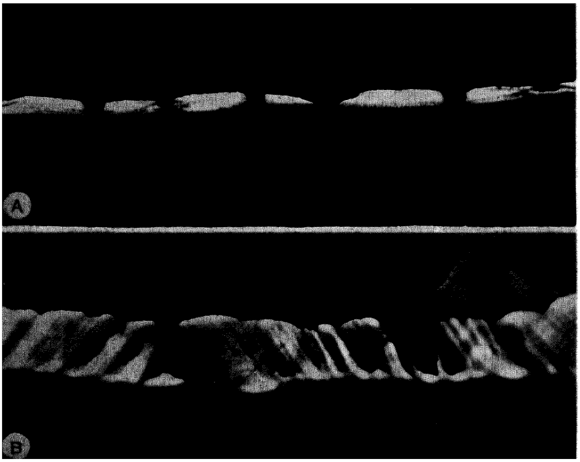

Fig. 34. Orientation of fibrils in the secondary wall of cotton: (A) A mature fiber photographed between crossed nicols to show bands of extinction. Magnification ×130. (B) Slightly swollen fibers showing reversal in direction of spiral of the fibrils. Magnification ×310.

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[19] Fibrils have an S spiral if, when the fiber is held in a vertical position, the spiral of the fibrils conforms in slope to the central portion of the letter S, and a Z spiral if the slope conforms to the central portion of the letter Z.

[20] H. Wakeham and N. Spicer, *Textile Research J.*, 21, 187 (1951).

The nature of the primary wall and the orientation of the fibrils in the secondary wall are two structural characteristics of cotton which play an important role in fiber swelling. Because the bulk of the fibrils in the secondary wall are oriented at an acute angle with respect to the long axis of the fiber, swelling is ordinarily greater transversely than lengthwise. Consequently, when raw mature cotton fibers are placed in certain swelling media, expansion of the cellulose in the secondary wall often causes the primary wall to burst. As the expanding cellulose pushes its way through these tears in the primary wall, the latter rolls back in such a way as to form collars, rings, or spirals which restrict the uniform expansion of the fiber (Fig. 35A). Of equal interest is the fact that purified fibers, from which the primary wall has been removed by alkaline digestion, also exhibit irregular swelling (Fig. 35B). This behavior is especially likely to occur under borderline swelling conditions. In the purified fibers it is the wind-

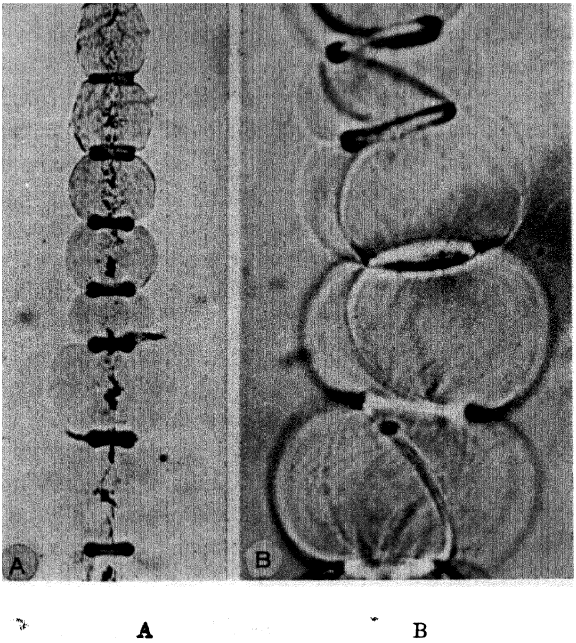

Fig. 35. Irregular swelling of cotton fibers in cuprammonium hydroxide solution: (A) Swollen unpurified fiber; Magnification ×100. (B) Swollen purified fiber in which the wax and pectic substances were removed by previous chemical treatments; magnification ×500.

ing which restricts lateral expansion. As changes in fiber width and length occur during swelling, the winding often assumes a more nearly transverse position and becomes clumped at various places along the fiber axis. Uniform lateral expansion of the fiber is then hindered because the winding does not expand freely in that direction. Although the primary wall is the chief cause of uneven swelling in raw fibers, even here the winding appears to influence swelling also, inasmuch as clumped fibrils as well as shreds of the primary wall are sometimes present at the constrictions.

(b) **Wood Fibers.** The commercially important types of wood may be placed in two general groups, namely, coniferous and deciduous. Those in the first group, commonly called softwoods, are obtained from conifers, i.e., evergreen or needle-leaved trees, and include such familiar types as spruce, pine, hemlock, and fir. The second group, or hardwoods, comprises the wood of those dicotyledons which are broad-leaved deciduous trees, such as oak, ash, maple, and chestnut. For practical as well as scientific reasons it is helpful to separate these two groups, inasmuch as they show distinguishing anatomical characteristics and have different industrial uses.

All woods are built up of cells or fibers, which differ widely with respect to size, form, and other microscopical characteristics.[21,22] A single sample of wood pulp ordinarily consists of several types of cells each of which shows considerable variation in dimensions. These several types, which perform different functions in the plant, vary also depending on growing conditions during different seasons of the year. Thus, those cells which develop rapidly during the spring growing season are larger and have thinner walls and broader central canals than those produced later in the season. Notwithstanding these variations, the fibers of the softwoods are significantly longer than those in hardwoods, averaging 3 mm. in length as compared with 1 mm.[23] Generally, also, the fibers of softwoods are wider. Besides fiber length and width, other dimensional properties of practical importance are the size of the lumen and the thickness of the wall.

Softwood is comparatively simple and homogeneous, consisting of only a few cell types.[21] The greater part (85–95%) of it consists of tracheids.[24] These are elongated single cells with more or less pointed ends, thick lignified walls, and usually many prominent bordered pits (Fig. 36). The lumen or central canal is large and empty. In cross section, tracheids look rectangular or polygonal. Besides tracheids, softwood also contains short, thin-walled prismatic parenchyma cells.

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[21] A. J. Eames and L. H. McDaniels, *Introduction to Plant Anatomy*, 2d ed., McGraw-Hill, New York, 1947.

[22] G. J. Ritter, *Tappi*, **32**, 11 (1949).

[23] E. Hägglund, *Chemistry of Wood*, Academic Press, New York, 1951.

[24] H. P. Brown in L. E. Wise and E. C. Jahn, eds., *Wood Chemistry*, 2d ed., Reinhold, New York, 1952, Vol. 1, Chapter 2, pp. 7–71.

Hardwoods are characterized by a complexity far greater than that of softwoods. This complexity is due to the presence of more kinds of cells (vessels, tracheids, fibers, parenchyma cells, and others), a broader distribution of sizes, wider variations in wall thickness, and a greater variety of arrangements of the cell types with respect to each other. Vessels are characteristic of hardwoods. These are long, wide, tubular structures, which arise from the transformation of a row of cells into a single duct. They show considerable diversity in size, wall thickness, type of pitting, nature of their perforations, and in their inclusions. The markings displayed by the walls of vessels are described as annular, spiral, reticulate, or pitted. Many hardwoods also contain tracheids resembling those in softwoods, but usually with thicker walls and bordered pits which are smaller and more generally distributed. True wood or libriform fibers are relatively narrow, long, and pointed and have very thick walls with inconspicuous pits. Parenchyma cells, which comprise a comparatively small part of

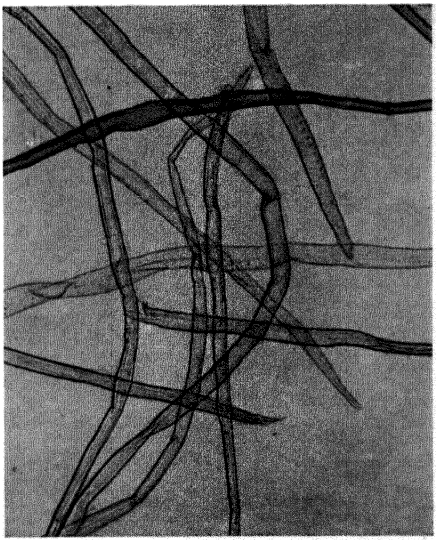

Fig. 36. Cells from a softwood. Magnification ×50. (Courtesy of Paper Section, National Bureau of Standards.)

domestic hardwoods, are typically short, thin-walled, prismatic cells with simple pits. Between the thick-walled fibers which give the wood strength and rigidity and the thin-walled elements adapted primarily to conduction of liquids, various intergrading forms occur (Fig. 37).

The principal structural features of typical wood fiber cells are illustrated in Figure 38, which is a sketch adapted from Bailey.[25] As in other native cellulose fibers, the thin outermost layer is called the primary wall. It consists of a system of cellulose fibrils plus relatively large amounts of noncellulosic organic substances such as lignin and pectin. The primary wall is usually weakly birefringent. The thick secondary wall which contains, besides cellulose, much lignin and other noncellulosic material, is commonly divided into an outer, a central, and an inner zone. The outer and inner zones are narrow: the central zone is comparatively broad.[23,26] The fibers as they exist in woody tissue are held together by an isotropic noncellulosic layer called the middle lamella.[27] The object of pulping is to

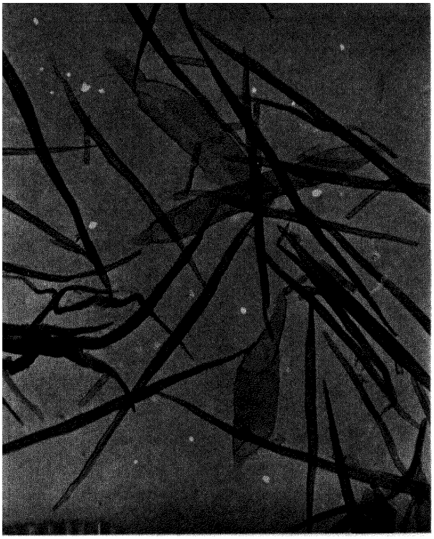

Fig. 37. Cells from a hardwood. Magnification ×50. (Courtesy of Paper Section, National Bureau of Standards.)

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[25] I. W. Bailey, *Ind. Eng. Chem.*, **30**, 40 (1938).

[26] I. W. Bailey and E. E. Berkley, *Am. J. Botany*, **29**, 231 (1942).

[27] W. M. Harlow in L. E. Wise and E. C. Jahn, editors, *Wood Chemistry*, 2d ed., 1952, Vol. 1, Chapter 4, pp. 99–116.

separate these cells from each other, and, usually, to remove the noncellulosic components.

Owing to the variety of cell types which occur in wood, it is difficult to describe their fine structure in generalities. At high magnification, for example, the secondary wall in many wood fibers is made up of concentric layers, as it is in cotton, but radial and other more complex designs also occur in certain woods. Although these patterns can sometimes be studied in specimens which have received no special preparation, ordinarily a treatment such as swelling is necessary in order to reveal them. It is evident, however, that regardless of other dissimilarities in configuration of the cell walls, the cellulose is always present as fibrils. Although a variety of physical and chemical treatments reveal the presence of fibrils, probably no method gives a more convincing demonstration of their presence than microdissection. When the fibers are dissected with microneedles, the fibrils which make up the wall can be separated from one another.[28,29] These fibrils are birefringent and show sharply defined extinction angles.

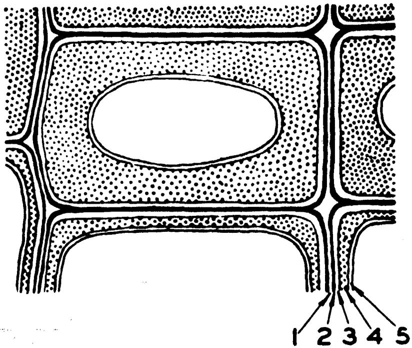

Fig. 38. Schematic representation of transverse section of wood fiber cells (according to Bailey[25]): (1) intercellular substance; (2) primary wall; (3) outer layer of secondary wall; (4) central layer of secondary wall; (5) inner layer of secondary wall.

In addition to direct visual observation of the fibrils themselves, there are other methods of study which are indicative of their presence and of their orientation. Among these are the observation of cracks brought about by mechanical stressing and by planes of hydrolysis produced during acid

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[28] W. Seifriz and C. W. Hock, *Paper Trade J.*, **102**, 36 (May 7, 1936).

[29] C. W. Hock and W. Seifriz, *Paper Trade J.*, **110**, 31 (Feb. 1, 1940).

or enzymatic degradation.[30-32] The deposition of crystals and metal particles[30,33,34] within the cellulose matrix is also helpful in investigating fibril structure, as well as being informative about the size and shape of pores, cavities, and channels through which chemical reagents penetrate the cellulose. A comparison of x-ray diagrams with microscopical data serves as a further confirmation of the orientation of the fibrils.[35] Investigations along these lines have shown that although the orientation of the fibrils in the secondary walls of wood fibers varies, a frequent condition is that in which the fibrils of the inner and outer layers of the wall lie nearly transverse and the fibrils in the central layer are more or less parallel to the long axis of the cell.[23,26,36,37] The orientation is dependent on a number of factors, among which are species, growth conditions, method of pulping, and degree of chemical refinement.[38,39] Since cellulose swells considerably in planes at right angles to the long axis of the fibrils and only slightly in a plane parallel to this axis, the orientation of the fibrils in wood fibers, as in cotton, favors irregular swelling or ballooning, even in purified fibers from which lignin and other noncellulosic constituents have been removed. However, the more severely the fibers have been treated during purification, the less pronounced is this swelling phenomenon.[40]

Lignin may occur in the middle lamella, the primary wall, and the secondary wall of wood fibers. As demonstrated by Bailey and Kerr,[41] in heavily lignified walls it is possible to remove the cellulose and leave a coherent residue of lignin or, conversely, to remove the lignin and leave the cellulose. Studies of this sort lead to the viewpoint that the fiber wall consists of a

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[30] I. W. Bailey, in F R. Moulton, ed., *The Cell and Protoplasm*, Science Press, Lancaster, 1940, pp. 31–43

[31] I. W. Bailey and M. R. Vestal, *J. Arnold Arboretum*, **18**, 196 (1937).

[32] R. Y. Stanier, *Bact. Revs.*, **6**, 143 (1942).

[33] A. Frey-Wyssling, *Protoplasma*, **25**, 261 (1936); **26**, 45 (1936); **27**, 372, 563 (1937).

[34] C. W. Hock and H. Mark in Emil Ott, editor, *Cellulose and Cellulose Derivatives* (High Polymers, Vol. V), Interscience, New York–London, 1943, Chapter III, Section E, pp. 346–351.

[35] C. W. Hock in W. Seifriz, editor, *The Structure of Protoplasm*, Iowa State College Press, Ames, Iowa, 1942, pp. 11–21; R. D. Preston, *The Molecular Architecture of Plant Cell Walls*, Wiley, New York, 1952.

[36] H. F. Lewis, *Tappi*, **33**, 418 (1950).

[37] E. Treiber, *Protoplasma*, **40**, 367 (1951).

[38] W. A. Sisson and G. L. Clark, *Ind. Eng. Chem., Anal. Ed.*, **5**, 296 (1933); G. L. Clark, *Tappi*, **33**, 108 (1950).

[39] A. B. Wardrop, *Textile Research J.*, **22**, 288 (1952).

[40] C. H. Carpenter and H. F. Lewis, *Paper Trade J.*, **99**, 37 (July 19, 1934).

[41] I. W. Bailey and T. Kerr, *J. Arnold Arboretum*, **18**, 261 (1937).

system of cellulose fibrils surrounded by lignin and other organic compounds. Differences in the visible patterns of the walls are attributable to variations in the orientation and aggregation of the fibrils and to the kind, amount, and arrangement of noncellulosic substances which are deposited between the fibrils.

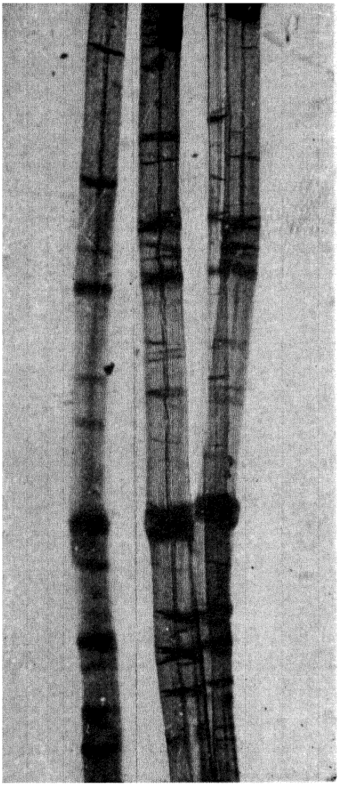

Fig. 39. "Dislocations" in flax fiber cells. Stained with zinc chloride–iodine solution. Magnification ×200.

(c) **Bast Fibers.** The principal bast fibers of commerce are flax, hemp, ramie, and jute. Separation of ramie fibers from the woody part of the stem is a difficult operation which is usually carried out by hand. The other three fibers are freed from the stem by a process known as retting. The length of the fibers ranges from a few inches to over a foot. Whereas the cotton fiber is a single plant cell, the bast fibers as obtained from the plant and as used in textiles are made up of many individual cells.[42] A characteristic of these cells is the occurrence of "dislocations" on their surfaces.[43] These markings, which are preferential places of attack when the fibers are placed in reagents, become especially prominent upon treatment with zinc chloride–iodine solution (Fig. 39). In flax, hemp, and sometimes in ramie, these transverse markings form the letter X, but this does not occur in jute.

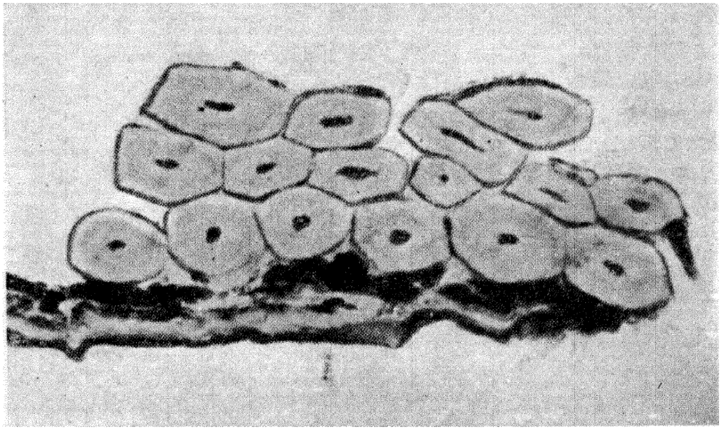

Fig. 40. Cross section of a flax fiber (Herzog[43]). Part of the "bark" remains attached to a group of flax cells. Magnification ×330.

At the tip of a growing flax stem all the cells are essentially alike. They are relatively small and uniform and have a tenuous primary wall only. A short distance back from the growing point the cells that are to develop into fibers increase in dimensions, and deposition of the secondary wall is initiated.[44] As observed in cross section (Fig. 40), a bundle of mature fiber cells is seen to consist of polygonal cells with straight smooth sides, which probably account for some of the luster associated with linen. Owing to the thickness of the secondary wall, the lumen of the cells is reduced to a narrow canal. When flax cells are swollen in cuprammonium hydroxide solution, iodine and sulfuric acid, and certain other reagents,[45,46] the layered structure of the secondary wall becomes increasingly prominent. The number of these layers varies, as many as fifty occurring in some cells.[44] A greater number of layers occurs in those fiber cells located at the base of the stem than in those at the growing tip.

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[42] A. J. Turner, *J. Textile Inst.*, **40,** P857 (1949); **40,** P972 (1949).

[43] A. Herzog, *Die Unterscheidung der Flachs und Hanffaser*, J. Springer, Berlin, 1926.

[44] C. W. Hock, *J. Research Natl. Bur. Standards*, **29,** 41 (1942).

Alternating layers of the secondary wall differ in their affinity for dyes and also in their brightness between crossed nicols. The layered pattern is due to dissimilarities in the density of alternate layers of cellulose and also to the presence of noncellulosic layers. The latter, which are especially prominent around the lumen, stain similarly to the primary wall and, as judged by staining behavior, appear to contain substances of a pectic nature.

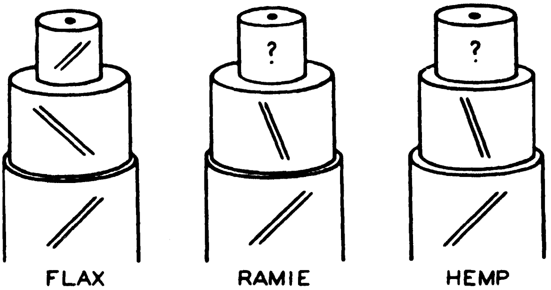

Fig. 41. Schematic representation of the orientation of fibrils in different layers of bast fibers (according to Roelofsen[47]).

When flax fibers are swollen in suitable reagents it is also evident that the cellulosic layers are subidvided into fibrils which are only a few tenths of a micron in diameter. That these fibrils spiral in different directions in the various bast fibers has been known for a long time. However, a comparison of the original literature reveals many contradictory data on the direction of spiral. Recently, Roelofsen[47] summarized the earlier literature on this subject and reinvestigated the spiral structure of flax, hemp, and ramie fibers. His results are depicted in Figure 41. As the sketch shows, the fibrils in the outermost layer of the secondary wall of all of these fibers make a Z spiral, whereas those in the broad central zone make an S spiral. An inner difficultly discernible Z spiral has been verified in flax, but is still conjectural in the others. Individual cells from each of these bast fibers

[45] C. R. Nodder, *J. Textile Inst.*, **13**, T161, T213 (1922).

[46] D. B. Anderson, *Am. J. Botany*, **14**, 187 (1927).

[47] P. A. Roelofsen, *Textile Research J.*, **21**, 412 (1951).

are similar in many respects. Minor differences in cell size, shape, wall thickness, and surface markings do, however, make it possible to identify them by microscopical techniques.[48–51]

(2) *Breakdown Structures of Native Cellulose*

The structure of cellulose is probably the most important as well as the least understood of the factors which influence the course of cellulose reac-

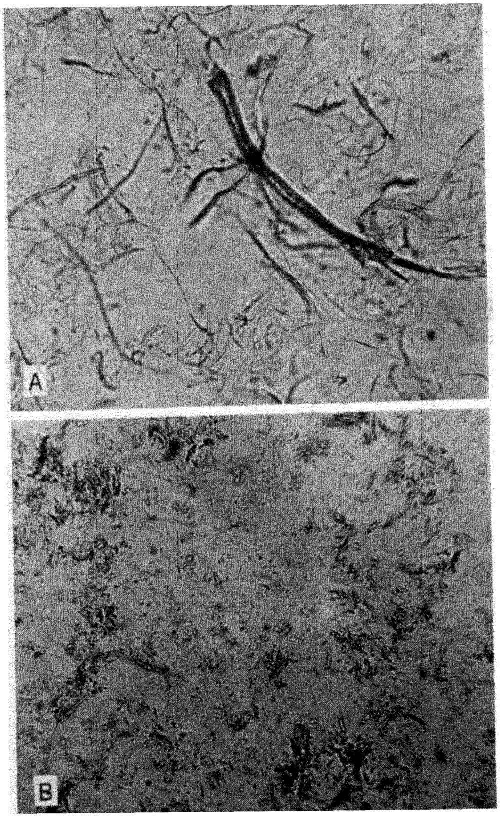

Fig. 42. Cotton fibers broken down by mechanical action: (A) after passage, while wet, through a Wiley mill; (B) after wet-grinding in a ball mill. Magnification ×100. See text p. 364.

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[48] T. F. Hanausek, *The Microscopy of Technical Products*, Wiley, New York, 1907.

[49] A. C. Whitford in H. R. Mauersberger, editor, *Matthews' Textile Fibers*, 5th ed., Wiley, New York, 1947, Chapter IX, pp. 305–368.

[50] T. M. Plitt, U. S. Dept. Commerce, *Circ.* C423 (1939).

[51] Am. Soc. Testing Materials, *Standards on Textile Materials*, Philadelphia, 1951.

tions. Some of the changes which cellulose undergoes during various treatments were perforce included in the foregoing discussion of its microscopical structure. Other changes, brought about by the action of physical, chemical, and biological agents, are discussed below. Aside from being of considerable interest in themselves, microscopical observations of these changes afford an additional source of information regarding fiber structure.

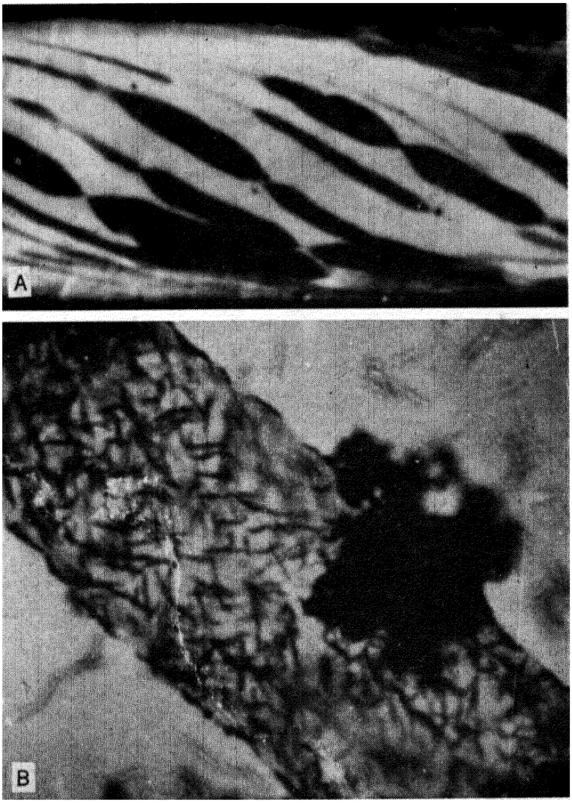

Fig. 43. Cellulose fibers attacked by biological organisms: (A) wood fiber degraded by the enzymatic activity of a fungus. Magnification ×280 (Bailey and Vestal[31]); (B) cotton fiber attacked by cellulose-decomposing bacteria. Magnification ×775 (Stanier[32]). See text p. 364.

(a) **Physical Treatments.** Many physical treatments such as grinding and beating lead to the separation of cellulose fibers into their component fibrils. That beating causes fibrillation is well known to the papermaker, who takes advantage of this behavior to enhance bonding. The extent of breakdown depends on the severity of treatment. For example, fibrillation is more pronounced after wet-grinding than after dry-grinding,[52,53] presumably because the swelling which occurs in water is sufficient to bring about some preliminary disruption in the interfibrillar regions. Figure 42A illustrates the appearance of cotton after passage, while wet, through a Wiley mill. Split-up of the fibers into fibrils is obvious. After more intensive mechanical treatment, as exemplified by prolonged action in a ball mill, the cellulose is present as short, narrow, rodlike particles, suggesting that the more vigorous milling has broken down the long fibrils into shorter lengths (Fig. 42B).

(b) **Biological Action.** The degradation of cellulose by biological agents, and the prevention of such deterioration, is a problem of major interest. Although this subject is treated more fully in Chapter III-C-5, a few statements about this type of breakdown and its relation to fiber structure are appropriate here. The manner in which certain fungi attack wood fibers has been described by Bailey and Vestal.[31] Owing to the action of these wood-destroying fungi, the cellulose is eaten away so as to leave hollow spaces within the cellulose framework (Fig. 43A). It is obvious from the photograph that attack has not occurred randomly, but in a manner which reflects the fibrillate structure of the cell wall. Likewise, the work of Stanier[32] on bacterial decomposition of cellulose shows that there is a close relationship between the avenues of attack and the structure of the cotton fiber. The position of the bacteria parallels the long axis of the fibrils, thereby presenting a crisscross appearance which corresponds to the known reversals between the outermost layer and the inner layers of fibrils in the secondary wall (Fig. 43B). The initial attack of cellulolytic organisms and of enzymes prepared from them is believed to occur preferentially in the amorphous regions of the cellulose,[54–56] often resulting in breakdown of the fibers into fibrils.

(c) **Chemical Reaction.** As already mentioned in the discussion of the microscopy of cotton, wood pulp, and bast fibers, the behavior of cellulose in chemical reagents figures prominently in the elucidation of fiber structure. Chemical swelling agents have been especially helpful in this respect. Moreover, swelling changes, for example those which result from mer-

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[52] P. H. Hermans and A. Weidinger, *J. Am. Chem. Soc.*, **68**, 1138 (1946).

[53] P. H. Hermans and A. Weidinger, *J. Am. Chem. Soc.*, **68**, 2547 (1946).

[54] R. Blum and W. H. Stahl, *Textile Research J.*, **22**, 178 (1952).

[55] C. S. Walseth, *Tappi*, **35**, 233 (1952).

[56] W. Kling and H. Mahl, *Melliand Textilber.*, **33**, 32 (1952).

cerization of cellulose by solutions of sodium hydroxide and from conversion of cellulose to alkali cellulose in the preparation of certain derivatives, have important commercial applications.

When cellulose is placed in sufficiently concentrated alkali, for example in an 18% NaOH solution, the reaction which occurs is commonly spoken of as mercerization. Fibers which have been treated in this way show an increase in tensile strength, an improvement in luster, and a greater affinity for certain dyes. Mercerized and unmercerized fibers are different in their microscopical appearance.[48,57,58] Although cotton staple fibers are ordinarily like flat twisted ribbons, after mercerization they resemble cylindrical hairs and are free of twist (Fig. 44). Mercerization is accompanied by increases in fiber diameter and cell-wall thickness, and by decreases in lumen breadth and fiber length. In a sample of fuzz fibers treated with an 18% NaOH solution, measurements revealed an 84% increase in fiber diameter, a 170% increase in wall thickness, and a reduction in the bore of the central

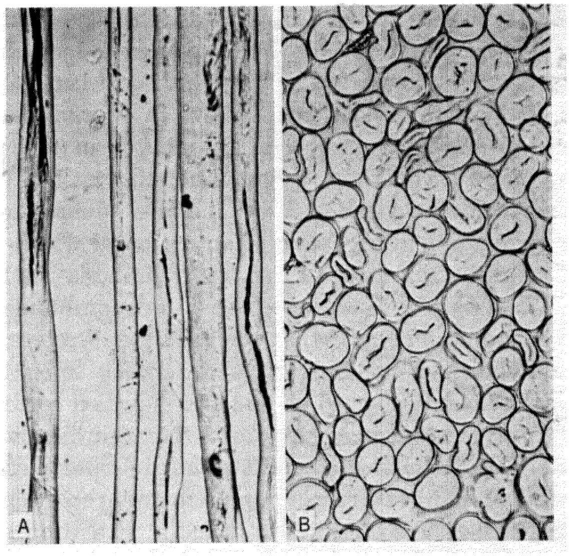

Fig. 44. Mercerized cotton fibers: (A) longitudinal view; (B) cross-sectional view. Magnification ×325. (Courtesy of the Institute of Textile Technology, Charlottesville, Va.)

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[57] T. L. W. Bailey in H. R. Mauersberger, editor, *Matthews' Textile Fibers*, 5th ed., Wiley, New York, 1947, Chapter VI, pp. 198–229.

[58] J. T. Marsh, *Mercerizing*, Chapman and Hall, London, 1941.

canal to 66% of its original width. The decrease in the amount of crystalline material and the increase in available surface, attendant upon swelling, greatly enhance the chemical reactivity of the cellulose.

Cuprammonium hydroxide solution is used not only as a solvent in making regenerated fibers but also as a means for dispersing cellulose in order to study certain of its physical and chemical properties. The point of view generally held by cellulose chemists, and supported by considerable experimental evidence, is that the properties, such as viscosity, of cuprammonium solutions of cellulose are attributable to the presence of long-chain molecules of the carbohydrate.[59] On the other hand, Farr and her collaborators[60–64] have claimed that cellulose does not dissolve in cuprammonium solution but maintains a visible state of aggregation in the form of ellipsoidal particles measuring 1.5 by 1.1 microns. It is claimed that each of these particles is surrounded by cementing material which swells in cuprammonium solution, thereby giving rise to a gel-like structure upon which characteristic properties of the dispersion depend. Farr's hypothesis has not been confirmed.[65–67] When cotton fibers are placed in cuprammonium reagent, microscopical examination shows that the cellulose dissolves, leaving residues whose amount and structure vary depending upon the extent of purification of the fibers[66] (Fig. 45, A and B). Purified cotton from which both waxy and pectic substances have been removed dissolves completely in the reagent. It is concluded, therefore, that microscopically resolvable particles of cellulose do not persist in cuprammonium solution and that the concept of fiber structure, according to which a cementing material binds ellipsoidal particles together to form fibrils, is not tenable.

The visible changes which cellulose undergoes in acid media are more varied than those produced by alkaline agents. Except for swelling, mild action causes few visible changes. Even after hydrolytic treatments which reduce the chain length considerably, the gross fiber structure may be retained, although the tensile strength is reduced. The extent of degradation caused by acids can often best be recognized by supplementary treatments such as crushing or swelling in alkaline solutions. A wood pulp fiber which was treated with 80% H_3PO_4 and then crushed on the microscope slide is shown in Figure 46A.[29] Separation of the fiber into fibrils is evident. Removal of the alkali-soluble portions from hydrolyzed cotton may leave a skeleton in which the spiral structure of the original cotton fiber is still recognizable.[68] Often, acid-hydrolyzed fibers also break down along transverse planes. Unlike unhydrolyzed fibers, the fibrils in hydrolyzed cellulose split up into shorter, although usually elongated, pieces (Fig. 46B). The size of these fibril fragments and the ease with which they separate depend on the severity of the hydrolysis. As the intensity of the acid treatment increases, the size of the particles into which the cellulose breaks down de-

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[59] C. W. Hock and H. Mark in Emil Ott, editor, *Cellulose and Cellulose Derivatives* (High Polymers, Vol. V), Interscience, New York-London, 1943, Chapter III, Section C, pp. 293–315.

[60] W. K. Farr, *Contribs. Boyce Thompson Inst.*, **10**, 71 (1938).

[61] W. K. Farr and S. H. Eckerson, *Contribs. Boyce Thompson Inst.*, **6**, 189 (1934).

[62] W. K. Farr, *J. Phys. Chem.*, **42**, 1113 (1938).

[63] J. Compton, *Contribs. Boyce Thompson Inst.*, **10**, 113 (1938).

[64] W. A. Sisson, *Contribs. Boyce Thompson Inst.*, **10**, 57 (1938).

[65] R. L. Whistler, A. R. Martin, and M. Harris, *J. Research Natl. Bur. Standards*, **24**, 555 (1940); *Am. Dyestuff Reptr.*, **29**, 244 (1940); *Textile Research*, **10**, 269 (1940).

[66] C. W. Hock and M. Harris, *J. Research Natl. Bur. Standards*, **24**, 743 (1940); *Am. Dyestuff Reptr.*, **29**, 287 (1940); *Textile Research*, **10**, 323 (1940).

[67] E. Heuser and J. W. Green, *Ind. Eng. Chem.*, **33**, 868 (1941).

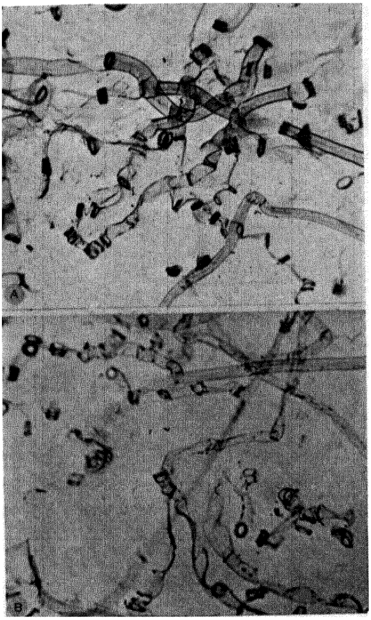

Fig. 45. Residue remaining after treatment of cotton fibers with cuprammonium reagent: (A) residue from unpurified fibers; (B) residue from dewaxed fibers. Magnification ×60.

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[68] K. Hess, *Die Chemie der Zellulose und ihrer Begleiter,* Akadem. Verlagsgesellschaft. Leipzig, 1928.

creases, and smaller particles, variously described as dermatosomes,[69] fusiform bodies,[22] spheroids, and others are produced.[37] Since severe hydrolysis leads eventually to the dissolution of cellulose and the formation of glucose, it might be expected that cellulose would break down into particles of decreasing size until soluble glucose was reached. Sometimes particles of this sort have been considered to be fundamental building units of constant dimensions. However, because of the diversity of magnitude assigned to each of these types, the apparent dependence of their characteristics on specific experimental conditions, and the uncertainties sometimes involved in their microscopical resolution, it seems more probable that they should be regarded as random cleavage particles rather than structures indicative of the fundamental architecture of cellulose. It is clear, however, that hydrolysis, like other reactions, proceeds in a manner which is influenced by the microstructure of the fiber. The most outstanding characteristic of this structure is the fibrillate nature of the cellulose.

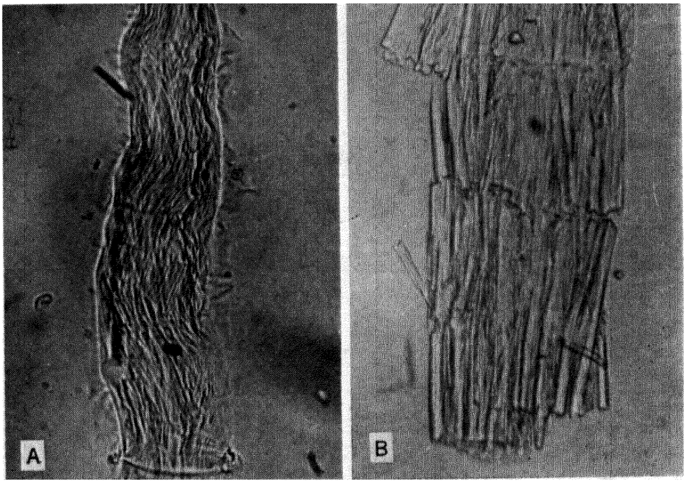

Fig. 46. Cellulose fibers degraded by acids: (A) separation of wood pulp fiber into fibrils on treatment with H_3PO_4; (B) hydrolyzed ramie fiber after treating with dilute alkali and crushing lightly to show transverse splitting. Magnification ×240.

(b) ELECTRON MICROSCOPICAL INVESTIGATION

During the last decade, electron microscopy has contributed significantly to our knowledge of the structure of cellulose. Although all native cellulose appears to be resolvable by light microscopy into a system of fibrils whose diameters are a few tenths of a micron, the electron microscope reveals that these comparatively coarse fibrils are made up of still finer ones. The results of the many investigators who have applied this new technique to the study of cellulose frequently differ in detail, but the basic conclusion to be drawn from this work is that in the range of small dimensions capable of direct visualization at the high resolving power of the electron microscope, native cellulose still shows an unquestionably fibrillate structure.

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[69] J. Wiesner, *Die Elementarstruktur*, A. Holder, Vienna, 1892.

(*1*) *Preparation of Specimens*

In order to understand and evaluate better the results of electron microscopical studies, a few general statements about the preparation of specimens may be helpful. In the first place, single fibers cannot be examined directly because specimens can be no thicker than several tenths of a micron. Since a generally satisfactory method for cutting ultrathin sections of native cellulose has not been available, electron microscopists have resorted to physical treatments such as beating, grinding, and ultrasonic vibration[53,57,70–81] and to chemical treatments such as the action of acids and alkalies [82–88] in order to obtain specimens of suitable dimensions.

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[70] R. B Barnes and C. J. Burton, *Ind Eng. Chem* , **35,** 120 (1943).

[71] A. Frey-Wyssling and K Muhlethaler, *Textile Research J* , **17,** 32 (1947).

[72] P H Hermans, *Textile Research J* , **16,** 545 (1946).

[73] K. Hess, H Kiessig, and J Gundermann, *Z physik Chem* , **B49,** 64 (1941).

[74] C. W. Hock and W G. Kinsinger, *Melliand Textilber.*, **31,** 43 (1950); *Chem. Zentr.*, **1950, I,** 1298

[75] E Husemann and A Carnap, *J makromol Chem* , **1,** 158 (1944).

[76] H. Jentgen, *Jentgen's Kunstseide u Zellwolle,* **23,** 76 (1941); *Chem. Abstracts,* **36,** 4331 (1942)

[77] W. G. Kinsinger and C. W. Hock, *Ind. Eng Chem* , **40,** 1711 (1948).

[78] K. Muhlethaler, *Biochim et Biophys Acta,* **3,** 15 (1949); *Chem. Zentr.* (Russian Zone Ed.), **1949, II,** 818

[79] G. R Sears and E A. Kregel, *Paper Trade J* , **114,** 43 (March 19, 1942).

[80] E. Steurer, K. Hess, and H Fromm, *Kolloid-Z* , **98,** 148 (1942).

[81] K. Wuhrmann, A. Heuberger, and K. Mühlethaler, *Experientia,* **2,** 105 (1946); *Chem. Abstracts,* **40,** 4219 (1946).

[82] O. Eisenhut and E. Kuhn, *Angew. Chem.*, **55,** 198 (1942).

[83] B. Eriksson and S. Saverborn, *Acta Agr. Suecana,* **11,** 233 (1946); *Brit. Abstracts,* **1948,** BII, 600.

[84] E. Husemann, *J. makromol. Chem.*, **1,** 16 (1943).

[85] E. Kuhn, *Melliand Textilber.*, **22,** 249 (1941); *Chem. Abstracts,* **35,** 7707 (1941).

[86] H. Ruska and M. Kretchmer, *Kolloid-Z.*, **93,** 163 (1940).

[87] W. Wergin, *Biol. Zentr.*, **63,** 350 (1943).

[88] W. Wergin, *Kolloid-Z.*, **98,** 131 (1942).

Although the thickness of fibers precludes direct viewing of their surfaces, this can be achieved indirectly through the use of replicas. Many procedures suitable for replicating fiber surfaces[77,89–95] and cross sections[96] have been described, but all of them consist essentially of making a suitable imprint of the fiber in a plastic film which is thin enough to be examined in the instrument. Another technique worthy of mention because of its widespread use and value is metal shadowing. Briefly, this consists of vaporizing a metal of high atomic weight onto the specimen in such a way that the various thicknesses of metal deposited on the surface produce different opacities to electrons and thereby enhance contrast in the image.[94–98] Recent electron microscopical examinations of cellulose, practically all of which have been carried out on metal-shadowed specimens, give a much more detailed and accurate picture of cellulose than was obtained earlier with unshadowed preparations.

(2) *Structure of Native Sources of Cellulose*

The electron microscope reveals that all native cellulose is built up in the same general manner. Whether it comes from industrially important sources such as cotton, wood, and flax, from the walls of algae, such as *Valonia*, or from unicellular organisms such as bacteria, it is composed of fibrils of the order of a few hundred Angstroms in diameter.[99] The diversity of fibril diameters, ranging all the way from fifty to several hundred Angstroms, which have been reported in the literature, is probably accounted for by such factors as (1) dissimilar techniques of specimen preparation, which influence the extent of separation of individual fibrils, their degree of swelling, and the amount of erosion; (2) contrast in the image, depending on whether or not the specimens were metal-shadowed; (3) uncertainties of instrument calibration; and (4) innate differences among celluloses

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[89] I. W. Fischbein, *J. Applied Phys.*, **21**, 1199 (1950).

[90] A. J. Hodge and A. B. Wardrop, *Nature*, **165**, 272 (1950).

[91] W. Kling and H. Mahl, *Melliand Textilber.*, **31**, 407 (1950); *Chem. Abstracts*, **44**, 9680 (1950).

[92] R. Signer, *Bull. soc. chim. France*, **1949**, 663.

[93] R. Signer, H. Pfister, and H. Studer, *Makromol. Chem.*, **6**, 15 (1951).

[94] R. W. G. Wyckoff, *Electron Microscopy: Technique and Applications*, Interscience New York-London, 1949.

[95] F. F. Morehead, *Textile Research J.*, **22**, 379 (1952).

[96] W. Kling and H. Mahl, *Melliand Textilber.*, **33**, 328 (1952).

[97] R. C. Williams and R. C. Backus, *J. Applied Phys.*, **20**, 98 (1949).

[98] R. C Williams and R. W. G. Wyckoff, *J. Applied Phys.*, **17**, 23 (1946).

[99] R. D. Preston, *Discussions Faraday Soc.*, No. **11**, 165 (1951).

of different origins. Although all fibrils may not have uniform and constant diameters, at least in a given specimen they vary within narrow limits. That the fibrils are quite long but of indefinite length is generally agreed upon.

The fibrils in primary and secondary walls are essentially similar but they are arranged differently. In primary walls they are comparatively poorly oriented. As shown in Figure 47, which is an electron micrograph of the primary wall of cotton, their arrangement gives the appearance of a loose irregular network.[15,36,78,100,101] Tripp and Rollins[16] detected this network in fibers as young as 3 days, but it appeared to be more distinct and more closely felted in older fibers. In recent studies, Kling and Mahl[102,103] and Roelofsen[10,11] describe a lengthwise orientation of the fibrils in that part of the primary wall which lies next to the structureless surface coating of waxy and pectic materials, and a more or less transverse orientation of fibrils on the inner side. By examining surface replicas of cotton before

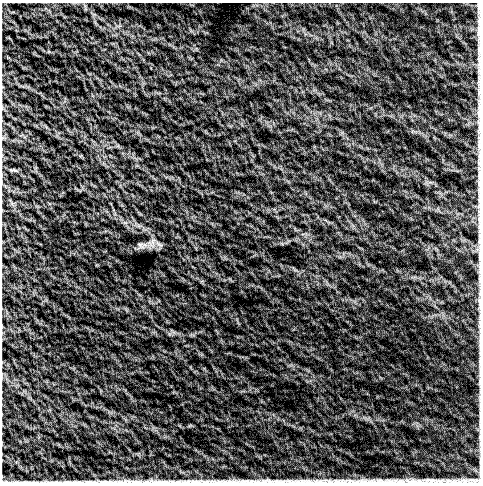

Fig. 47. Purified primary wall of cotton. Electron micrograph of gold-shadowed specimen. Magnification ×15,000 (Tripp, Moore, and Rollins[15]) (USDA Photo by Southern Regional Research Laboratory).

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[100] A. Frey-Wyssling, K. Mühlethaler, and R. W. G. Wyckoff, *Experientia*, **4**, 475 (1948).

[101] A. J. Hodge and A. B. Wardrop, *Australian J. Sci. Research*, **3**, 265 (1950).

[102] W. Kling and H. Mahl, *Melliand Textilber.*, **32**, 131 (1951); *Chem. Abstracts*, **45**, 4931 (1951).

[103] W. Kling and H. Mahl, *Melliand Textilber.*, **33**, 829 (1952).

and after solvent extraction, alkaline cooking and chlorine bleaching, the former[102] were able to follow the pitting and gradual removal of the primary wall which occurred during these treatments. By proper commercial purification procedures, the primary wall is completely removed, thereby exposing the fibrils in the secondary wall[77] (Fig. 48).

Electron micrographs of cellulose from the secondary wall of cotton, wood pulp, and ramie are shown in Figures 49A, B, and C. The fibrillate nature of the cellulose is obvious in all of the micrographs, although there are small differences in texture which may be characteristic of cellulose from a particular source. The fibrils in ramie, for example, are somewhat coarser and also straighter and smoother than those in either cotton or wood pulp. In contrast to the condition in the primary wall, the fibrils in secondary walls are arranged more or less parallel to each other. The examination of replicas of fiber surfaces[77,92] and of sections[89,90,101] is especially suitable for demonstrating cell-wall organization. Studies of this sort confirm that in the secondary wall the fibrils are aligned in parallel to form layers and that interfibrillar regions occupy only a comparatively small part of the wall.

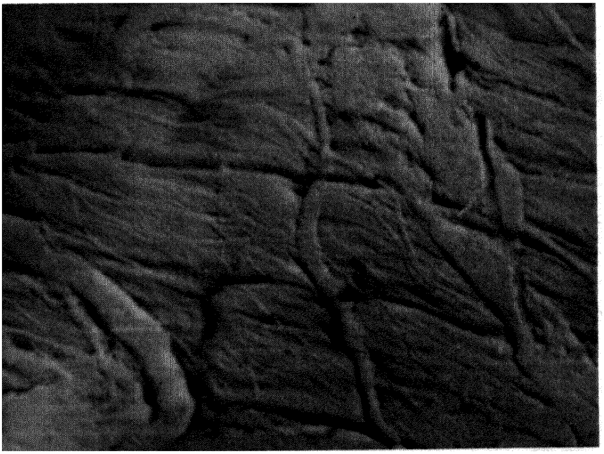

Fig. 48. Surface of purified cotton fiber. Electron micrograph of chromium-shadowed replica. Magnification ×15,000.

Noncellulosic constituents such as pectin, lignin, and hemicellulose may occupy spaces between the fibrils in both primary and secondary walls. Removal of these noncellulosic components from the cell walls seems not to disturb the remaining cellulose fibrils. Extraction of pectin from the primary wall of cotton, for example, leaves a network of cellulose fibrils, whereas removal of the cellulose leaves a coherent residue of pectin[16,56] (Fig. 50, A and B). In specimens of unpurified wood, the fibrils give the impression of being embedded in a matrix; in specimens from which the lignin has been removed, the fibrils are more sharply defined.[101] Re-

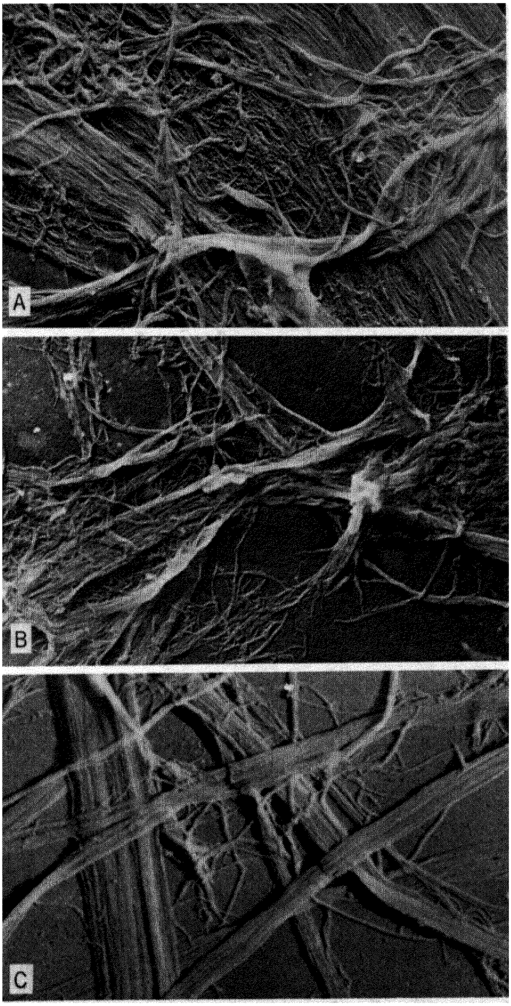

Fig 49. Cellulose from the secondary wall: (A) cotton; (B) wood pulp; (C) ramie. All fibers wet-beaten in Waring Blendor; electron micrographs of specimens shadowed with chromium. Magnification ×13,500.

moval of the cellulose leaves a residue of lignin. Mühlethaler[78] has shown that in sisal the lignin which remains is present as thin layers containing many fine pores through which the cellulose fibrils evidently had passed. Pictures of this sort give no indication of any close chemical bond between the amorphous lignin and the oriented cellulose fibrils. According to Rånby,[104,105] the hemicellulose of wood is diffuse, in contrast to the structurally well defined cellulose.

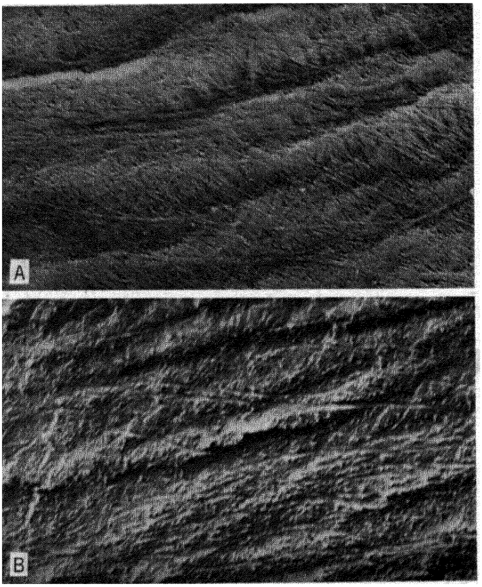

Fig. 50. Primary wall of the cotton fiber. Electron micrographs of metal-shadowed replicas: (A) after removal of pectin by enzymatic action; (B) after removal of cellulose by enzymatic action. Magnification ×15,000 (Kling and Mahl[56]).

(3) *Chemical Breakdown of Native Cellulose*

The behavior of cellulose during chemical reactions and the influence of the structure of cellulose on the course of these reactions have been studied with the electron microscope. As might be expected, the specific breakdown picture depends on the type and severity of the reaction. Figure 51 is a micrograph of alkali-treated wood pulp cellulose. The purified pulp was

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[104] B. G. Rånby, *Svensk Papperstidn.*, **55**, 115 (1952).

[105] B. G. Rånby, *Tappi*, **36**, A8 (1953).

first shredded by wet-beating, whereupon the specimens for electron microscopy were placed in solutions of 18% NaOH for several minutes. The fibrils appear to have been distorted somewhat by the alkali treatment but, nevertheless, the fibrillate pattern is still fairly well preserved during this early stage of the reaction.[106] Similarly, in specimens of partially xanthated fibers in which the reacted regions were tagged with a metal having high

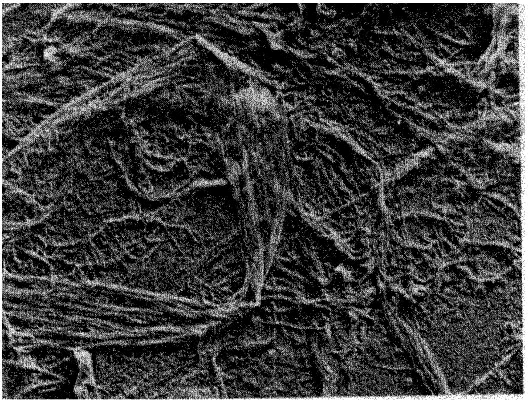

Fig. 51. Alkali-treated wood pulp cellulose. Electron micrograph of chromium-shadowed specimen. Magnification ×14,000.

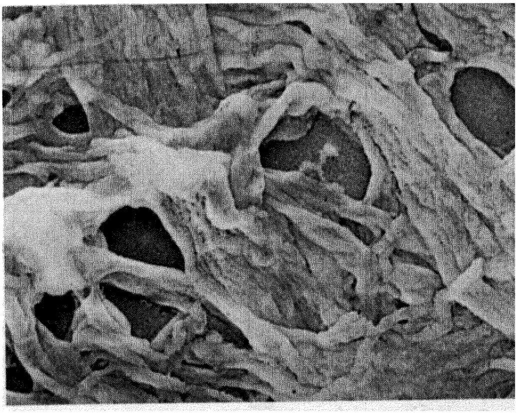

Fig. 52. Swollen fibrils in cotton cellulose whose crystallinity was reduced by treatment with ethylamine. Electron micrograph of chromium-shadowed specimen. Magnification ×35,000.

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[106] C. W. Hock, *Textile Research J.*, **20**, 141 (1950).

opacity to electrons, thereby accomplishing for electron microscopy what is comparable to differential staining of objects for light microscopy, the distribution of reacted regions bore a relationship to the fibrillate structure of the original cellulose. Cotton cellulose whose crystallinity was reduced to 25% by treatment with ethylamine, according to the method of Segal, Nelson, and Conrad,[107] is shown in Figure 52. In comparison with untreated cellulose (Figure 49), the fibrils have swollen to several times their original diameter.

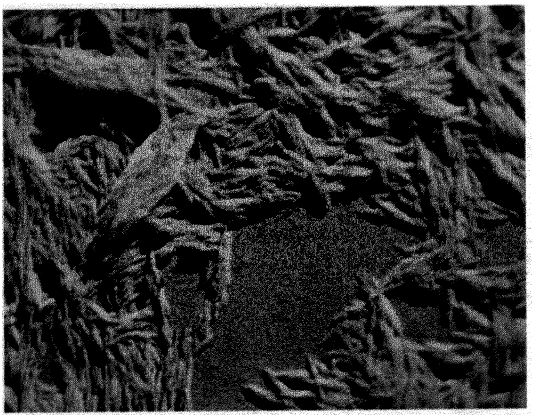

Fig 53. Hydrolyzed cotton cellulose. Electron micrograph of chromium-shadowed specimen. Magnification ×28,000.

Particular attention has been directed to the changes which cellulose undergoes upon treatment with acids. Fibril fragments from cotton cellulose which had been hydrolyzed for 2 hours in 2.5 *M* HCl–0.6 *M* $FeCl_3$ and then prepared for electron microscopical examination by grinding in water, are illustrated in Figure 53. The needlelike bodies are approximately 2500 A. long and 150 A. wide.[106] Mukherjee and coworkers[108] obtained essentially similar results with ramie and cotton cellulose. Likewise, in length distribution curves of the rod-shaped fragments resulting from hydrolytic degradation of ramie and cotton, Husemann and Carnap[109] detected a maximum at 2250 ± 250 A. After acid treatments of cotton, Signer[92] observed fusiforms which were 100 A. wide and several thousand Angstroms long. The rodlike particles with a length of 500 to 600 A. and a width of 50 to 100 A., which Rånby and Ribi[110,111] found in different celluloses after acid degradation, were related by them directly to the micelles postulated from earlier x-ray investigations. After hydrolyzing fiber samples down to their limiting degree of polymerization, i.e., the point beyond which further acid treatment reduces the length of the cellulose chain only very slowly, Morehead[112] placed the hydrolyzed cellulose in water and subjected it to ultrasonic vibrations. A nice correlation was demonstrated between the average length of the elongated particles observed in the electron microscope and the length of the crystallite as calculated from data on degree of polymerization.

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[107] L. Segal, M. L. Nelson, and C. M. Conrad, *J. Phys. & Colloid Chem.*, **55**, 325 (1951).

[108] S. M. Mukherjee, J. Sikorski, and H. J. Woods, *Nature*, **167**, 821 (1951).

[109] E. Husemann and A. Carnap, *Naturwissenschaften*, **32**, 79 (1944).

(4) Correlation of Microscopical and X-Ray Diffraction Data

Electron microscopy has shown beyond question that native cellulose has a fundamentally fibrillate structure. X-ray diffraction studies, already discussed in an earlier section, have given rise to a structural model according to which there are some regions of cellulose in which the molecules are ordered, i.e., crystalline, and other regions in which they are disordered, i.e., amorphous. How can these concepts be resolved in arriving at an explanation of the small-scale structure of native cellulose?

In the first place, it should be recalled that owing to the uncertainties which arise in interpreting the x-ray diffraction diagrams, the dimensions reported for the crystalline regions indicate only the order of magnitude. The problems which arise in evaluating the diffraction diagrams of cellulose and the assumptions required in order to calculate the size of the ordered regions have been discussed by Bunn,[113,114] Hermans,[115] Meyer,[116] van der Wyk,[117] Hock,[118] and others. In estimating the size of the crystalline regions from the breadth of the x-ray interferences it has generally been assumed, among other things, that the ordered regions are small, that they

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[110] B. G. Rånby and E. Ribi, *Experientia*, **6**, 12 (1950); *Chem. Abstracts*, **44**, 4677 (1950).

[111] B. G. Rånby, *Tappi*, **35**, 53 (1952); B. G. Rånby, *Discussions Faraday Soc.*, No. **11**, 158 (1951).

[112] F. F Morehead, *Textile Research J.*, **20**, 549 (1950).

[113] C. W. Bunn, *Chemical Crystallography*, Clarendon Press, Oxford, 1945.

[114] C W. Bunn in J. M. Preston, editor, *Fibre Science*, The Textile Institute, Manchester, 1949, Chapter 11, pp. 158–180.

[115] P. H. Hermans, *Physics and Chemistry of Cellulose Fibres*, Elsevier, New York, 1949.

[116] K. H. Meyer, *Natural and Synthetic High Polymers*, 2d ed., Interscience, New York-London, 1950.

[117] A. J. A. van der Wyk and K. H. Meyer, *Kolloid-Z.*, **120**, 9 (1951)

[118] C. W. Hock, *J. Polymer Sci.*, **8**, 425 (1952).

have relatively definite boundaries, and that they possess perfect three-dimensional regularity. Calculations, then, lead to the conclusion that in ramie, for example, there are rod-shaped crystallites about 60 A. wide and at least 600 A. long. Such values are, however, only averages; they tell nothing about the distribution of crystalline regions, and they do not prove the existence of individual crystalline particles. Moreover, if there is some disorder within those regions—a condition which seems highly probable—the dimensions would be larger than those actually calculated. Hence the values given in the literature are only minimum ones for the size of the ordered regions.

The probable arrangement of crystalline and noncrystalline regions in terms of the fibrillate structure of cellulose has received the attention of several investigators. According to the interpretation of Frey-Wyssling,[119,120] the fiber is made up of fibrils having diameters of 150 to 250 A. These fibrils, in turn, consist of flat crystalline micellar strands from 60 to 90 A. wide. It is postulated, further, that the micellar strands are surrounded by "paracrystalline" (i.e., imperfectly crystalline) cellulose which is responsible for aggregating them into fibrils. The entire fibril, i.e., a bundle of micellar strands embedded in imperfectly crystalline cellulose, is also surrounded by a cortex of imperfectly crystalline cellulose.

Another interpretation has been advanced by some investigators,[71,81,83,90,121] who point to the apparent correspondence between the comparatively narrow, approximately 60 A.-wide fibrils which have been reported from some electron microscopical studies and the same width value which, as a result of x-ray diffraction work, has been assigned to the ordered regions of cellulose. Other electron microscopists have, however, described fibrils which are several times this minimum width, i.e., a few hundred Angstroms wide. It seems that these broader fibrils might also be identified with the crystallites previously inferred from x-ray examination.[90,101,116,118,122] Especially does this seem likely, when one recalls that the determination of exact fibril width is beset with some uncertainties and also that the values derived from x-ray diffraction should not be taken too literally. In this connection, the concept of Meyer,[116,123] according to which the fibril has an approximate crystalline regularity except for gradual

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[119] A. Frey-Wyssling, *Makromol. Chem.*, **6**, 7 (1951).

[120] A. Frey-Wyssling, *Science*, **119**, 80 (1954).

[121] B. G. Rånby, *Fine Structure and Reactions of Native Cellulose*, Thesis, Uppsala, 1952.

[122] R. D. Preston, E. Nicolai, R. Reed, and A. Millard, *Nature*, **162**, 665 (1948).

[123] K. H. Meyer, *Melliand Textilber.*, **33**, 485 (1952).

continuous deformations, seems to offer a satisfactory picture of the arrangement of the macromolecules within the fibril.[90,94,118,122] Such an interpretation places the emphasis on the visible fibrils rather than on structures inferred from x-ray diffraction. Furthermore, it is interesting to note that the x-ray diffraction data can be accounted for by either small, highly crystalline nuclei or by larger regions of intermediate, but relatively uniform, order.

Although even in the so-called amorphous parts there is probably some degree of order,[124] there are nevertheless regions which are more accessible than others, because of either their less perfect or less dense molecular arrangement. The fibrils themselves are relatively resistant to attack. On the other hand, the comparative ease with which a wide variety of degradative reactions proceeds in the interfibrillar regions and along the fibril surfaces, suggests that much of the accessible cellulose is situated in those regions. The specific breakdown picture depends, of course, on the type and severity of treatment. Following intensive treatments, such as strong acid hydrolysis, the fibrils sometimes split transversely. It is tempting to infer from this type of observation the presence of more or less individualized morphological islands of crystalline cellulose surrounded by amorphous material. However, for reasons already mentioned and also because, subsequent to a variety of treatments, fibrillation occurs first and only later does transverse splitting occur, it seems more likely that the ordered regularity of the fibrils in the longitudinal direction is not interrupted by regions of the same magnitude and extent of disorder as those which occur between the fibrils.[118] Rather do the observations seem to support the idea that the fibrils are more or less uniform regions having intermediate or relatively high lateral order, except for certain distortions and irregularities which constitute points of weakness where attack on the fibrils continues.

2. Rayons

(a) LIGHT MICROSCOPICAL INVESTIGATION

(*1*) *Structure of Rayons*

Rayons are made by passing solutions of modified cellulose through an orifice and then solidifying them in the form of filaments. The properties of these man-made fibers are, accordingly, controllable within rather wide limits. Thus, the size of the filaments, their cross-sectional shape, the

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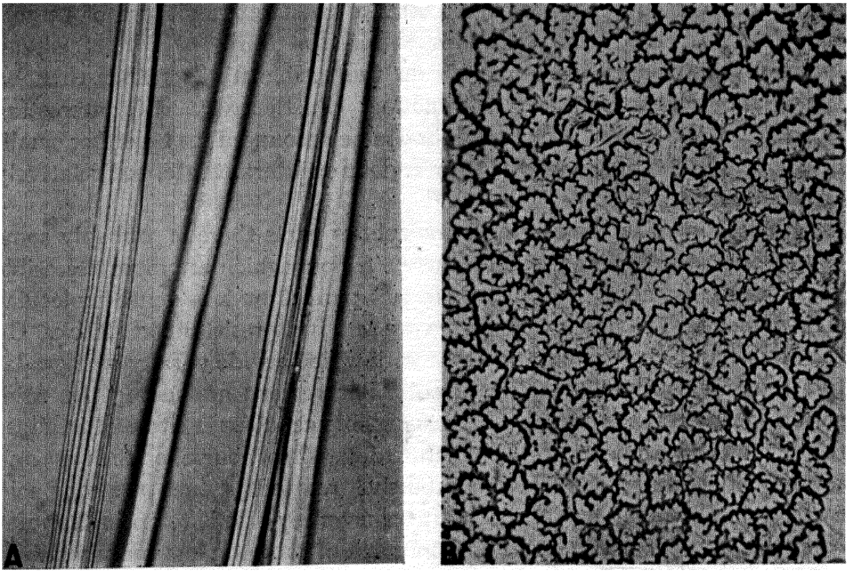
[124] O. Kratky, *Kolloid-Z.*, **120**, 24 (1951).



A B

Fig. 54. Viscose rayon fibers: (A) longitudinal view; (B) cross-sectional view. Magnification ×220.

nature of their surfaces, and their mechanical properties vary depending on the conditions of manufacture. Nevertheless, different types of rayon have certain distinguishing structural features which make microscopical examination the easiest, quickest, and often the best means of identification.[50,51,125,126–134]

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[125] W. Von Bergen and W. Krauss, *Textile Fiber Atlas*, new rev. ed., Textile Book Publishers, New York, 1949.

[126] E. M. Chamot and C. W. Mason, *Handbook of Chemical Microscopy*, Vol. 1, 2d ed., Wiley, New York, 1938.

[127] A. Herzog, *Die mikroskopische Untersuchung der Seide und der Kunstseide*, J. Springer, Berlin, 1924.

[128] W. Krauss in H. R. Mauersberger, editor, *Matthews' Textile Fibers*, 5th ed., Wiley, New York, 1947, Chapter XXII, pp. 977–1059.

[129] J. M. Preston, *Modern Textile Microscopy*, Emmott and Co., London, 1933.

[130] E. J. Saxl in H. R. Mauersberger and E. W. K. Schwarz, eds., *Rayon and Staple Fiber Handbook*, 3d ed., Rayon Handbook Co., New York, 1939, Chapter XVI, pp. 649–683.

[131] E. R. Schwarz, *Textiles and the Microscope*, McGraw-Hill, New York, 1934.

[132] J. H. Skinkle, *Textile Testing*, Chemical Publishing Co., Brooklyn, 1949.

[133] *Identification of Textile Materials*, 3d ed., The Textile Institute, Manchester, 1951.

[134] Synthetic Fiber Table, *Textile World*, **101**, 105 (1951).

Rayons ordinarily possess a high degree of luster. When dull fibers are desired, the manufacturing process includes some treatment for reducing luster. Usually this is accomplished by incorporating an opaque pigment, such as titanium dioxide, in the spinning solution. Where dullness is

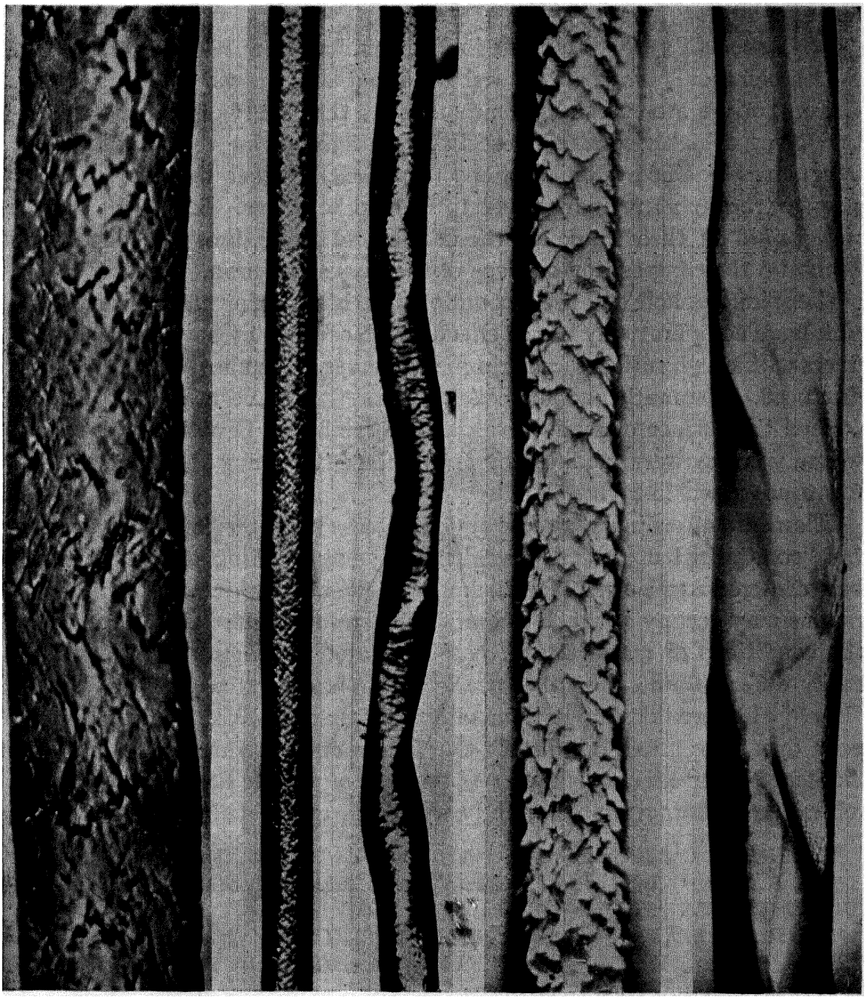

Fig. 55. Viscose rayon fibers whose surfaces were modified by appropriate stretching and setting during spinning. Magnification ×650 (Reumuth[139]).

achieved in this way, the microscope reveals dark specks of the delusterant scattered throughout the fiber. Observations made by dark-field illumination are especially useful in observing the distribution of the delustering reagent.[129,135]

(a) **Viscose Rayon.** As seen in longitudinal view, viscose rayon filaments commonly have a striated or fluted appearance (see Fig. 54A). Cross sections are especially characteristic, their chief distinguishing feature being a highly serrated or scalloped margin, owing to the presence of irregular, but shallow indentations (Fig. 54B). Fiber shapes vary from circular through irregularly oval to ribbonlike forms. The chief factors responsible for their shape are the nature and strength of the coagulating bath and the composition and age of the viscose solution. Size and shape of the spinneret hole and the amount of stretching during and after coagulation have comparatively minor effects.[136] However, by special processing, fibers with rough surfaces and crimp, sometimes resembling wool, have been produced. Reumuth and his collaborators[137-139] have examined and described the surface of many artificial textile fibers. Several viscose fibers whose surfaces were modified by appropriate stretching and setting treatments are shown in Figure 55.

Filaments of ordinary viscose rayon possess an outer "skin" and a central "core" which are readily revealed by dyeing, swelling, and examination between crossed nicols. The thickness of the skin, which in strong tough rayons may occupy as much as half of the cross-sectional area, depends on the conditions of manufacture. As illustrated by Figure 56, the skin is easily differentiated from the core by suitable dyeing techniques.[129,140,141] Usually the core takes up dyes more quickly than the skin, but once having been dyed, the latter retains the dye longer on subsequent washing.[140,142] Similarly, when filaments and cross sections of viscose rayon are placed in solvent acetylating mixtures, the core reacts and dissolves more quickly

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[135] A. Herzog, *Textil-Forsch.*, **3**, 1 (1921); *Chem. Zentr.*, **1921, IV**, 288.

[136] H. R. Mauersberger, editor, *Matthews' Textile Fibers*, 5th ed., Wiley, New York, 1947, Chapter XVIII, pp. 738–789.

[137] H. Reumuth, *Klepzig's Texil-Z.*, **39**, 612 (1936); *Chem. Zentr.*, **1937, I**, 761.

[138] H. Reumuth, W. Kling, and H. Schwerdtner, *Kunstseide u. Zellwolle*, **19**, 247 (1937); *Chem. Zentr.*, **1937, II**, 2930.

[139] H. Reumuth, *Kunstseide u. Zellwolle*, **21**, 286 (1939); *Chem. Abstracts*, **33**, 8414 (1939).

[140] P. H. Hermans, *Textile Research J.*, **18**, 9 (1948).

[141] F. F. Morehead and W. A. Sisson, *Textile Research J.*, **15**, 443 (1945).

[142] W. Schramek and J. Helm, *Kolloid-Z.*, **85**, 291 (1938).

than the skin.[143,144] Preston[145,146] explains the differential dye absorption of skin and core largely on the basis of higher orientation in the skin. According to Morehead and Sisson,[141] the formation of a skin is related more closely to the rate of crystallization of the cellulose in the spinning bath than it is to the orientation resulting from stretching. However, a completely satisfactory explanation of the cause and nature of the skin and core is still to be achieved. A fuller knowledge of the small-scale structure of viscose will undoubtedly be helpful in explaining this phenomenon.

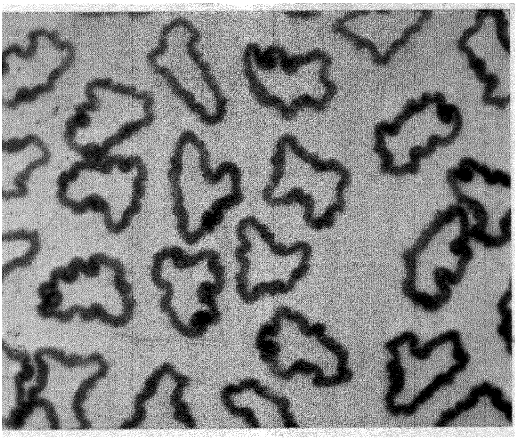

Fig. 56. "Skin effect" in viscose rayon (Morehead and Sisson[141]). Tire-cord yarn stained with Victoria blue and Calcomine yellow. Magnification ×550.

(b) **Cuprammonium Rayon.** Like viscose, cuprammonium rayon is a regenerated cellulose. Filaments of this rayon are particularly uniform in diameter, and as seen in the light microscope,[136] have smooth surfaces without markings of any kind (Fig. 57A). Cross sections are round or occasionally slightly oval (Fig. 57B). Cuprammonium filaments show no distinct differentiation into skin and core such as is found in viscose rayon.

The double refraction of regenerated cellulose is lower than that of native cellulose. Observations of the birefringence of regenerated fibers is some-

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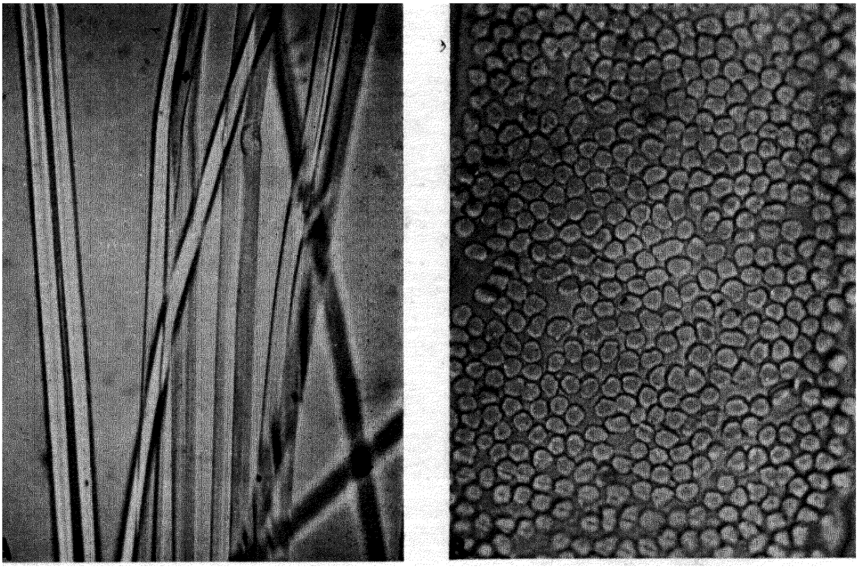
[143] H. Siebourg, *Zellwolle, Kunstseide, Seide*, **46**, 215 (1941); *Chem. Zentr.*, **1941, II,** 1463.

[144] A. Marschall and M. Stauch, *Jentgen's Kunstseide u. Zellwolle*, **25**, 112 (1943); *Chem. Abstracts*, **38**, 4797 (1944).

[145] J. M. Preston, *J. Soc. Chem. Ind.*, **50**, 199 (1931).

[146] J. M. Preston and G. D. Joshi, *Kolloid-Z.*, **122**, 6 (1951).

times of diagnostic value, as pointed out by several investigators.[147,148] Since the thick parts of fibers show higher orders of retardation colors with the polarizing microscope than do the thin parts, fibers with irregular cross-sectional shapes can be distinguished from those which are uniform. Thus, viscose with its serrated outline, shows alternating longitudinal bands of higher and lower order colors corresponding to its marginal indentations; a smooth round fiber such as cuprammonium rayon shows colors of progressively rising order from the edge to the center.



A B

Fig. 57. Cuprammonium rayon fibers: (A) longitudinal view; (B) cross-sectional view. Magnification ×220.

(c) **Acetate Rayon.** Cross sections of cellulose acetate rayon show two to four, occasionally more, smoothly rounded lobes which often give the sections a sort of clover-leaf shape. The lobed nature of acetate rayon easily distinguishes it from viscose which has more numerous shallow indentations. In longitudinal view the clefts between the lobes show up as pro-

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[147] L. G. Lawrie, *J. Soc. Dyers Colourists*, **44**, 73 (1928).

[148] A. Herzog, *Melliand Textilber.*, **21**, 97 (1940); *Chem. Abstracts*, **34**, 4578 (1940).

nounced striations running parallel to the long axis of the filament.[149] Sometimes the filaments have a broad twist.[51] The appearance of acetate rayon is illustrated in Figure 58, A and B.

Sometimes acetate rayon is hydrolyzed, i.e., saponified, in order to improve its strength or to achieve special effects during dyeing and finishing. Depending on the conditions, either partial or complete conversion of the cellulose ester to cellulose is effected. Microscopical methods afford an excellent means of appraising the extent of regeneration. Differential dyeing, followed by the examination of cross sections shows that in partially hydrolyzed rayon regeneration occurs mainly near the fiber surface, thereby giving rise to a layer which stains differently from the interior. Owing to differences in the refractive indices of saponified cellulose (1.54) and of cellulose acetate (1.47), phase contrast microscopy[150] also delineates these

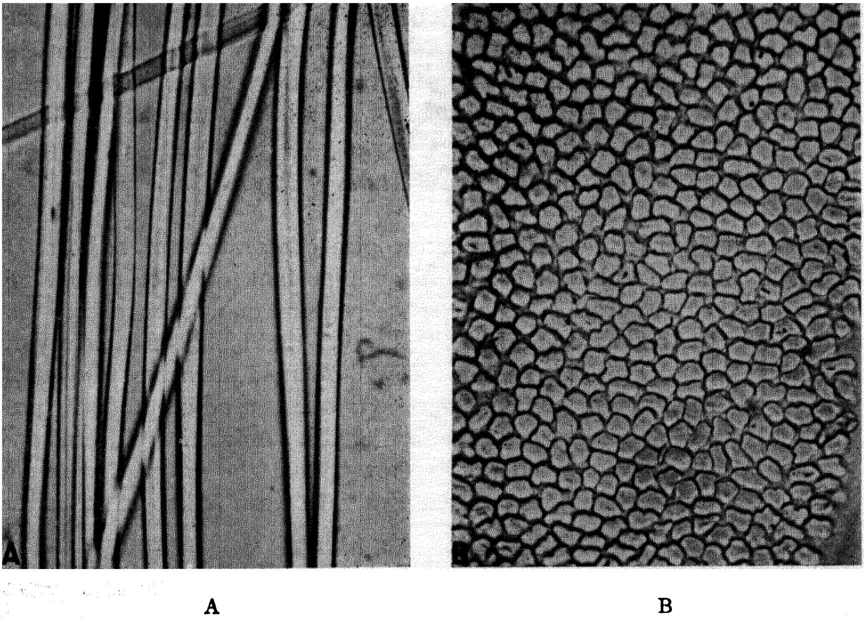

Fig. 58. Acetate rayon fibers: (A) longitudinal view; (B) cross-sectional view. Magnification X220.

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[149] H. DeW. Smith and H. R. Childs in H. R. Mauersberger, editor, *Mathews' Textile Fibers*, 5th ed., Wiley, New York, 1947, Chapter XIX, pp. 790–854.

[150] A. H. Bennett, H. Jupnik, H. Osterberg, and O. W. Richards, *Phase Microscopy, Principles and Applications*, Wiley, New York, 1951.

two regions.[151] Between crossed nicols, sections of surface-saponified acetate rayon show an inner, almost isotropic core surrounded by an outer layer which is strongly anisotropic.

The influence of structural order on the dyeing properties of saponified cellulose acetate rayon was studied by Work,[152] who applied to filaments of various degrees of order the differential dye test which Goldthwait and his associates[14] used successfully in separating mature and immature cotton fibers. He found that the dye acceptance of the filaments depended on the extent to which they had been stretched. Apparently these dissimilarities in dye uptake depend on the relationship between the size of the dye molecules and the variations in available space within the filaments.

(2) *Breakdown Structures of Rayon*

As in fibers of native cellulose, microscopical observations of the behavior of rayons during breakdown constitute an important source of information regarding their structure. Upon exerting pressure on swollen viscose filaments, Welch, Roseveare, and Mark[153] observed that highly oriented rayons split longitudinally into fibrils. In less well-oriented filaments, fibrillation was more difficult; the lateral connections between adjacent fibrils produced a kind of network. A comparison of x-ray diffraction patterns and the corresponding photomicrographs showed that the orientation of the fibrils parallels crystallite orientation which, in turn, is known to be dependent on spinning conditions.

In order to study the organization of rayons, Lovell and Goldschmid[154] compared the hydrolysis residues of regenerated cellulose filaments which differed only in degree of stretch. On controlled hydrolysis during which the acid removes the accessible noncrystalline cellulose, the rayons remained unchanged in appearance until treated mechanically, whereupon longitudinal and transverse splitting occurred. In rayons of low stretch the filaments broke down more or less randomly; in highly stretched rayon, fibrillation and sharp transverse splitting occurred. The regular breakdown of highly stretched samples, in contrast to the irregular breakdown of unstretched samples, is indicative of differences in orientation of the crystalline component of the samples.

In order to gain an insight into the microscopical structure of cellulose acetate rayon, Simmens and Howlett[155] examined filaments which had been fractured under tension. The fiber surfaces were without structure before rupturing but afterwards cracks inclined to the axis of the filament occurred. Internal cracking, itself a modification of the surface effect, was also observed. Between crossed nicols the stretched filaments showed a complex spiral pattern. Various pretreatments either reduced or increased the degree of cracking which occurred under tension, presumably by altering latent strains within the filaments. These results led to the conclusion that the surface layers of acetate rayon filaments differ from the inside in having lower extensibility.

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[151] F. F. Morehead, *ASTM Bull.*, **163**, 54 (1950).

[152] R. W. Work, *Textile Research J.*, **19**, 381 (1949).

[153] L. M. Welch, W. E. Roseveare, and H. Mark, *Ind. Eng. Chem.*, **38**, 580 (1946).

[154] E. L. Lovell and O. Goldschmid, *Ind. Eng. Chem.*, **38**, 811 (1946).

Additional comments on the breakdown structures of regenerated cellulose are included in the discussion of the electron microscopy of rayons which follows.

(b) ELECTRON MICROSCOPICAL INVESTIGATION

The electron microscope has amply demonstrated the fibrillate structure of native cellulose fibers. Rayon fibers have not been investigated so thoroughly with this instrument, but the available information indicates that they also frequently split into fibrils. The extent of fibrillation depends on the degree of orientation of the filaments. Fibrillation is, however, usually not so pronounced as in native cellulose, and there is greater variability of the fibril pattern.

Figure 59 is an electron micrograph of textile viscose rayon. The specimen was obtained by beating wet rayon filaments in a Waring Blendor. The fibrils have diameters of a few hundred Angstroms and appear to form a kind of irregular network, owing to lateral cohesion and crossing over of the fibrils. Longer fibrils and less frequent crossing over occur in high-tenacity tire-cord rayon.[156] Essentially similar results have been reported by other investigators[72,82,84,157–160] upon examination of different types of viscose. Various degrees of fibrillation, depending largely on the amount of stretch applied to the filaments during manufacture, have been described. Fibrillation remarkably similar to that in native fibers has been pictured by Ribi[161] in viscose that was subjected to ultrasonic vibrations. Although

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[155] S. Simmens and F. Howlett, *J. Textile Inst.*, **40**, T590 (1949).

[156] C. W. Hock, *Textile Research J.*, **18**, 366 (1948).

[157] A. Frey-Wyssling, *Makromol. Chem.*, **7**, 163 (1951).

[158] E. Husemann, *J. makromol. Chem.*, **1**, 158 (1944).

[159] E. Franz, F. H. Müller, and L. Wallner, *Forsch.-Ber. Zellwolle u. Kunstseide-Rings G.m.b.H.*, **1942**, No. 2, 75; *Chem. Zentr.*, **1942**, *II*, 1646.

[160] L. Wallner, *Melliand Textilber.*, **23**, 261 (1942); *Chem. Abstracts*, **37**, 775 (1943)

[161] E. Ribi, *Arkiv Kemi*, **2**, 551 (1950); *Chem. Abstracts*, **45**, 5923 (1951).

Mühlethaler[162] stresses that viscose fibers contain unaltered fragments o the original cellulose, i.e., cotton or wood, it seems certain that the regenerated cellulose itself is often fibrillate.

Electron microscopical observations of acid-hydrolyzed regenerated cellulose have been made by several investigators, particularly Morehead[11] and Ribi.[161] Whereas ultrasonic vibrations release comparatively long fibrils from the unhydrolyzed parent samples, the same treatment causes the hydrolyzed celluloses to break down into short fibrils or particles

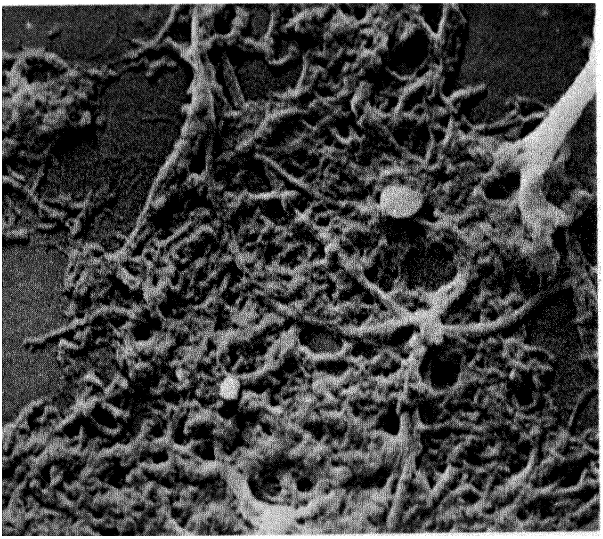

Fig. 59. Textile viscose rayon. Fibers wet-beaten in Waring Blendor. Electron micrograph of specimen shadowed with chromium. Magnification ×34,000.

These particles which are a few hundred Angstroms long and less than a hundred Angstroms wide, are smaller than the corresponding structures released from hydrolyzed native cellulose. Furthermore, their dimensions vary depending on the orientation and crystallinity of the sample. Thus, a highly crystalline and well-oriented tire-cord rayon yields larger particles than a low-stretch textile rayon. Notwithstanding that the size of the particles may be somewhat greater than that of the original crystallite (because recrystallization may occur during hydrolysis), the dimensions of the electron microscopically visible particles agree satisfactorily with the size of the crystallite as calculated from other data. These results have been considered to support the fringed micelle theory of cellulose structure (see Section B of this chapter).

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[162] K. Mühlethaler, *Experientia*, **6**, 226 (1950).

Cuprammonium rayon is shown in Figure 60. The fibrils released by wet-beating are rather similar to those from the viscose illustrated in Figure 59.

Specimens obtained by grinding rayon acetate filaments possessing different physical properties were examined electron microscopically by Work.[152] Without orientation no fibrillation took place. When the filaments were both oriented and highly crystalline, breakdown tended to be parallel to the fiber axis, thereby producing long fibrils. Fibrillation was even more pronounced when the oriented acetate was first saponified.

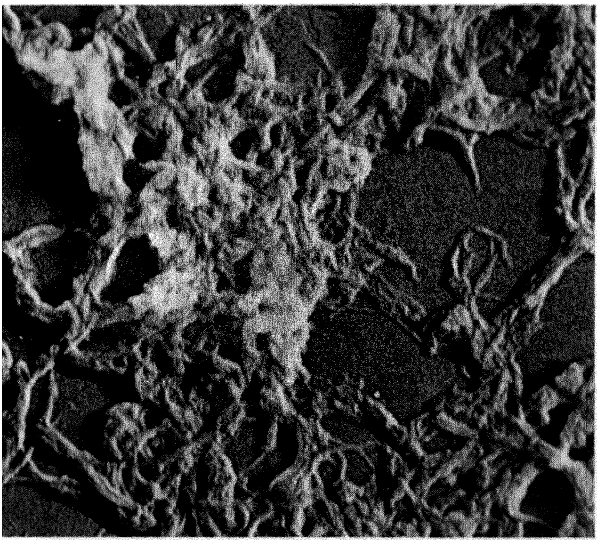

Fig. 60 Cuprammonium rayon. Fibers wet-beaten in Waring Blendor. Electron micrograph of specimen shadowed with chromium. Magnification ×34,000.

Some limited success has been achieved in the examination of cross sections of rayon filaments. Hermans,[163] for example, published an electron micrograph of a cross section of a viscose fiber from tire-cord yarn. Numerous small voids are shown in a rather thick cortical layer. Newman,[164] who sectioned cuprammonium, viscose, and regenerated acetate filaments, has published a micrograph of cuprammonium rayon. The pattern is essentially granular with a suggestion of a differentiation between skin and core. Further investigations of sections of rayon filaments will doubltess contribute to our knowledge of the structure of rayons.

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[163] P. H. Hermans, *Textile Research J.*, **20,** 105 (1950).

[164] S. B. Newman, *ASTM Bull.*, **163,** 57 (1950).

Electron microscopy of surface replicas of filaments reveals distinct differences among rayons of different types.[91–93,156,165] Chromium-shadowed nitrocellulose replicas of the surfaces of cuprammonium and viscose rayon fibers are shown in Figure 61. Except for occasional markings which give them a kind of scaly character, the cuprammonium fibers are relatively smooth—a condition probably contributing to their customary glossiness. The replicas of the textile viscose and the high-tenacity viscose rayon are

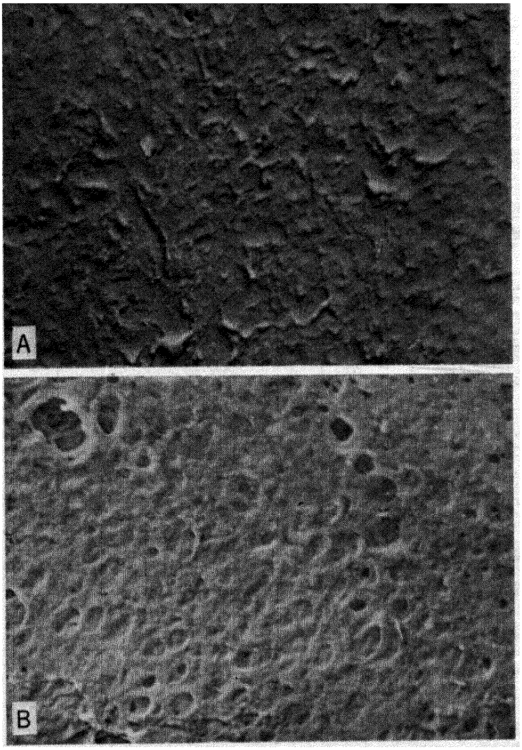

Fig. 61. Surface of rayon fibers: (A) cuprammonium rayon; (B) high-tenacity viscose rayon. Electron micrographs of chromium-shadowed replicas. Magnification ×40,000.

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[165] W. Kaye, *J. Applied Phys.*, **20**, 1209 (1949); V. Peck and W. Kaye, *Textile Research J.*, **24**, 295, 300 (1954).

more uneven and reflect a netlike structure. Although both the cuprammonium and the viscose fibers broke down into fibrils upon beating, their surfaces, unlike those of purified fibers of native cellulose, show little evidence of fibrils.

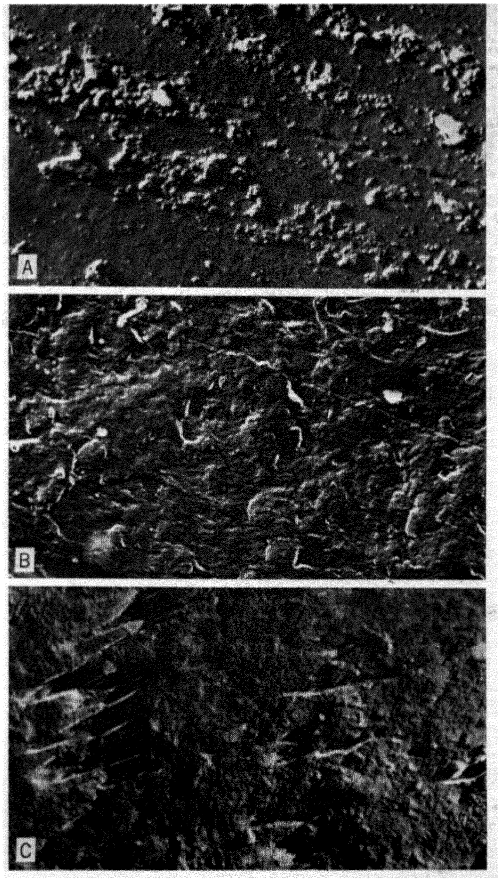

Fig. 62. Surface of cellulose acetate rayon fibers: (A) undrafted; (B) typical production fiber, which was drafted to 100 per cent elongation during the drying operation; (C) fiber similar to B, after breaking in tension. Electron micrographs of uranium-shadowed aluminum–beryllium alloy replicas. Magnification ×18,500 (Peck and Kaye[165]).

The surface of cellulose acetate fibers was studied by Peck and Kaye,[165] who obtained excellent results with aluminum–beryllium alloy replicas. The surface of an undrafted fiber, a drafted fiber, and a drafted fiber after breaking in tension are illustrated in Figure 62, A, B, and C, respectively. These studies showed that the fibers possess a highly oriented, but nonuniform, multilayered skin, whose thickness is influenced by the extent of drafting. Aside from revealing interesting structural dissimilarities between rayons, the replica method is a useful means for studying certain aspects of detergency,[102] dyeing,[166,167] and other processing treatments.

Although rayons have not been investigated so thoroughly as native cellulose fibers, nevertheless electron microscopy has demonstrated its usefulness as a technique capable of supplying fundamental information about the finer details of their structure. It is to be expected that additional knowledge gained through continued application of this method to fiber studies will contribute to the practical betterment of these man-made fibers.

[166] F. A Hamm and J. J. Comer, *Anal. Chem.*, **20,** 861 (1948)

[167] G. L. Royer and C. Maresh, *Textile Research J.*, **17,** 477 (1947)

D. STRUCTURE–SORPTION RELATIONSHIPS*

JOHN A. HOWSMON

1. Sorption Phenomena

Cellulose and cellulose derivatives are hygroscopic and when surrounded by an atmosphere containing the vapor of water or certain organic liquids will take up vapor from or lose vapor to the atmosphere until equilibrium is attained. The general process of interaction of a substance with a vapor atmosphere under any of a number of conditions is usually called sorption. The take-up of water or other vapor is called adsorption; the loss of water or other vapor occurring on reduction of the partial pressure is called desorption. The phenomenon is of importance because the presence of sorbed liquids changes the chemical behavior, mechanical properties, and electrical characteristics of cellulose. The chemical composition and submicroscopic structure of a material usually determine not only the amount of vapor adsorbed by the material, but also the manner in which and the extent to which this sorbed vapor affects the chemical and mechanical behavior of the system. Since most cellulose fibers have essentially constant chemical composition, the submicroscopic structure predominates in determining the course and effects of sorption; in cellulose derivatives, both chemical composition and structure must be considered. Although the general principles and theory of sorption developed in this chapter are not limited to water vapor specifically, the experimental data and discussion will stress water sorption because of the relative scarcity of data for other liquids.

(a) SORPTION ISOTHERMS

The data from sorption experiments are usually expressed either in the form of isotherms or isosteres. In an adsorption isotherm the amount of vapor adsorbed, or regain, is plotted against the pressure of the vapor in the surrounding atmosphere at constant temperature. The units most commonly used are grams vapor adsorbed per gram of dry cellulose and the relative vapor pressure of sorbate; that is, the relative humidity for the specific case of water sorption. In an adsorption isostere the relative vapor pressure of sorbate at which a given amount of vapor is adsorbed is plotted against temperature or frequently as log P versus 1/T. Isosteres are most important for the determination of thermodynamic data such as the heat of sorption; however, most data are taken isothermally and therefore the discussion here will be principally restricted to isotherms.

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* In this section has been incorporated pertinent material from E. I. Valko's section on "Sorption of Water and Other Vapors by Cellulose," which appeared in the original edition of this book on pages 379–423.

All cellulose and cellulose derivatives have characteristic sigmoid sorption isotherms similar to that shown in Figure 63 by the data of Urquhart and Williams[1] for kier-boiled cotton. At low relative humidity the amount of water adsorbed increases rapidly with increasing relative humidity. At moderate relative humidities the increase is smaller and approximately linear up to about 60% relative humidity. As the saturation pressure is approached, the amount of water adsorbed increases much more rapidly than the relative vapor pressure and the isotherm becomes almost parallel to the regain axis. Similar isotherms are found for water vapor and other high polymers including silk, wool, polyamides, casein, gelatin, and other proteins. The take-up of water by sulfuric and phosphoric acids follows a similar course.[2]

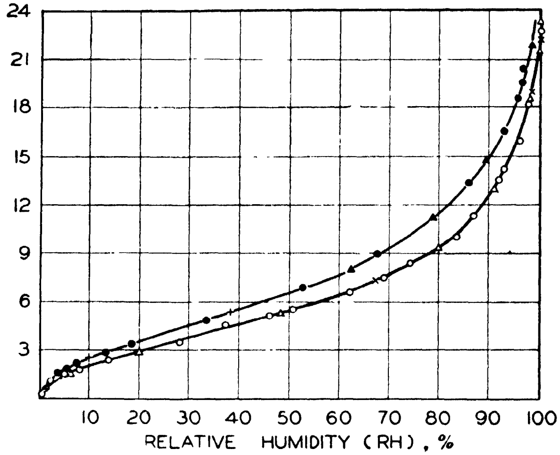

Fig. 63. Adsorption (lower) and desorption (upper) isotherms of kier-boiled cotton (Urquhart and Williams[1]). Ordinate, per cent moisture regain.

The hysteresis effect, also illustrated in Figure 63, arising from a sensitive dependence of the amount of water sorbed upon the previous sorption history of the sample is as characteristic of sorption isotherms of cellulosic and most other fibrous materials as is the shape of the isotherm. For water vapor, the isotherm obtained by placing a dry fiber successively in atmospheres of increasing relative humidity lies below that obtained by placing a wet fiber in atmospheres of decreasing relative humidity. These two sorption curves initiated from the completely dry and completely wet states respectively bound an equilibrium area. Any point within this area may be reached by starting from the correct initial state between the two extremes. For example, if a dry sample is conditioned at 60% relative humidity and then placed in surroundings of decreasing relative humidity until it is again dry, the transition to the desorption curve for a wet sample will not occur instantaneously. A new desorption curve will be obtained which for the most part will fall between the standard adsorption–desorption isotherms and approach the desorption isotherm only at relatively low humidities. The adsorption regain for a given relative humidity is usually of the order of 80 to 90 per cent of the desorption value.

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[1] A. R. Urquhart and A. M. Williams, *J. Textile Inst.*, **15**, T138, T433, T550 (1924); **16**, T155 (1925); **17**, T38 (1926).

[2] J. R. Katz, *Trans. Faraday Soc.*, **29**, 279 (1933).

(b) MECHANISM AND THEORIES OF SORPTION

The general topics of solvation (that is, the attachment of water molecules to dissolved particles) and of sorption (that is, the attachment of vapor molecules to sites in solids) have been extensively treated in the literature, especially since about 1940. A complete review cannot be given but specific reference should be made to the statistical adsorption concepts of Brunauer, Emmett, and Teller[3] as extended by Bull,[4] Cassie,[5] Dole,[6] and White and Eyring[7] as well as to the solution theories of Flory,[8] Huggins,[9] Rowen and Simha,[10] and Hailwood and Horrobin[11] and the excellent review by McLaren and Rowen.[12] At present no theoretical approach has adequately described the sorption of water by high polymers over the entire range of relative vapor pressures.

A satisfactory theory of sorption of vapors by cellulose must account for at least five major phenomena and related effects. These are: (1) the magnitude of the sorption; (2) the shape of the isotherm; (3) heat effects accompanying sorption; (4) swelling; and (5) hysteresis. The remainder of this discussion will therefore be devoted to a generalized mechanism of the sorption process itself and the probable nature of the associated phenomena.

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[3] S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

[4] H. B. Bull, *J. Am. Chem. Soc.*, **66**, 1499 (1944).

[5] A. B. D. Cassie, *Trans. Faraday Soc.*, **41**, 450 (1945).

[6] M. Dole, *J. Chem. Phys.*, **16**, 25 (1948); *J. Colloid Sci.*, **3**, 411 (1948).

[7] H. J. White, Jr., and H. Eyring, *Textile Research J*, **17**, 523 (1947).

[8] P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

[9] M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **44**, 431 (1943).

[10] J. W. Rowen and R. Simha, *J. Phys. & Colloid Chem.*, **53**, 921 (1949).

[11] A. J. Hailwood and S. Horrobin, *Trans. Faraday Soc.*, **42B**, 84 (1946).

[12] A. D. McLaren and J. W. Rowen, *J. Polymer Sci.*, **7**, 289 (1951).

In general, the various theories of sorption of water and other vapors by cellulose can be divided into two groups. The first group treats sorption principally as a surface phenomenon and the second group as a solution of the sorbate in a viscous medium. In treatments of sorption by cellulose by either group, special cellulose structure effects and special types of association between cellulose and water are usually assumed. The necessity of such assumptions is often questioned in view of the similarity between cellulose sorption phenomena and the sorption of vapors by such different materials as sulfuric acid and titanium dioxide for which special assumptions are unnecessary. There seems no doubt, however, that the sorption phenomena for cellulose are closely related to the order–disorder structure of cellulose fibers and that there are two distinct classes of sorbed water· (1) that which is "bound" to the cellulose with a bonding energy greater than that normally found for water, and (2) that which is condensed within the structure without heat effects above those of normal condensation.[13–15]

In the surface adsorption theories, the fiber is considered to have a large amount of internal surface which contains residual valences or polar groups which can strongly adsorb water. Sorption of water by interaction with the groups on the inner surface will account for the sorption isotherm below about 50% relative humidity but will not account for the rapid increase in sorbed water at higher relative humidities. In order to account for the high relative humidity end of the isotherm, various investigators have postulated that as the primary inner surface becomes covered with sorbed water, additional water is condensed in the structure by capillary condensation,[13,16] by adsorption in "multilayers,"[3,17] or by primary sorption on additional surfaces which become exposed for sorption as the structure swells or the temperature is changed.[18]

In treatment of sorption by solution theories, the cellulose fiber is treated as a system comprised of ordered regions embedded in a matrix of dis-

[13] F. T. Pierce, *J. Textile Inst.*, **20**, T133 (1929).

[14] E. Filby and O. Maass, *Can. J. Research*, **7**, 162 (1932)

[15] S. E. Smith, *J. Am. Chem. Soc.*, **69**, 646 (1947).

[16] S. E. Sheppard and P. T. Newsome, *Ind. Eng. Chem.*, **26**, 285 (1934).

[17] J. B. Babbitt, *Can. J. Research*, **20A**, 143 (1942).

[18] A. R. Urquhart, *J. Textile Inst.*, **20**, T117, T125 (1929).

ordered regions, and sorption is considered to be a process of solution of water in the disordered regions. There are primary sites capable of adsorbing water in the disordered regions, and the mixing of these regions with water in these regions is analogous to the dilution of sulfuric acid.[19] This concept is based on the fact that for some polymeric systems, such as cellulose nitrate–acetone,[10,20] a solution of the adsorbent occurs at high relative vapor pressures of the sorbate. In various cases the combination of cellulose and water has been considered as an ideal solid solution[11] or as a solution with large deviations from ideality because of restrictions on the swelling of the system by the insoluble ordered regions.[10,21] The latter case is most probable but in no case can the entire isotherm be attributed to solution effects alone.

Actually, the two classes of sorption theory, surface sorption and solution sorption, are not so different as they appear. Both classes postulate the presence of strong bonding sites for sorption and the addition of large amounts of normally condensed water in the swollen structure at high humidities. White and Eyring[7] have pointed out that the mathematical expressions for multilayer surface adsorption and for extremely imperfect solutions have the same form. The viewpoint taken in the following discussion contains elements of both theoretical approaches. Specific reference is made to the principles most adequately expressed by Rowen and Simha[10,21] and White and Eyring[7] and to the extensive treatment of sorption, swelling, and properties of cellulose fibers by P. H. Hermans.[22]

In the general case, cellulose fibers must be considered to be composed of macromolecules for which the packing varies from point to point within the fiber. In a region of high packing order, the molecules are held together by hydrogen bond formation between cellulose hydroxyls; in perfect crystalline regions most of the hydroxyls will be involved in hydrogen bonding. As the order decreases, the number of hydroxyl groups involved in hydrogen bonding with an adjacent cellulose molecule decreases so that in disordered regions a large number of the cellulose hydroxyls are not hydrogen bonded and can be considered free or accessible. The details of these structures have been discussed in detail in Section B of this chapter. It is now generally accepted that the unbonded cellulose hydroxyls, which may occur on the surface of a crystalline region, within an imperfect crystal, or throughout a disordered region, act as sorption centers capable of sorbing water with bonding energy greater than that in water. The first water adsorbed at low relative humidity is principally adsorbed by hydrogen bond formation with the unbonded hydroxyl groups of the cellulose fiber. As soon as water adsorption begins, even at low humidities the fiber starts to swell and the swelling continues as the cellulose is exposed to higher humidity atmosphere. This swelling of the fiber structure breaks hydrogen bonds between cellulose molecules so that the number of active sorption centers increases as more water is adsorbed. In any event, it is generally accepted that most of the water adsorbed by cellulose fibers up to about 60% relative humidity is adsorbed on unbonded hydroxyl groups which were present in the original sample or were freed by the rupture of secondary cellulose–cellulose bonds during the course of the adsorption and swelling.

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[19] J. J. Hermans in P. H. Hermans, *Contributions to the Physics of Cellulose Fibres*, Elsevier, New York, 1946, Appendix 1, pp. 188–194.

[20] J. W. McBain, S. J. Good, A. M. Baker, B. P. Davies, H. J. Willavorp, and R. Buckingham, *Trans. Far. Soc.*, **29B**, 1086 (1933).

[21] R. Simha and J. W. Rowen, *J. Am. Chem. Soc.*, **70**, 1663 (1948).

[22] P. H. Hermans, *Physics and Chemistry of Cellulose Fibres*, Elsevier, New York, 1949, Part 2, Chapters II and VI, Part 3, Chapter VIII.

As the relative humidity is increased beyond 50 to 60%, still more sorption sites are made available by progressive swelling of the fiber. The total number of hydroxyl groups capable of acting as active sorption centers is limited by the network structure of the fiber. The crystalline regions are not swollen in water, act as "cross-links," and restrict the formation of additional available hydroxyl groups by restricting the swelling of adjacent less crystalline portions of the structure. In any case the formation of new sorption centers by swelling will not alone account for the rapid rise in adsorption at high relative humidity. In this high humidity region, additional water is added as "multilayers"[3] or by solution of cellulose in water.[10,22] Either case will allow adsorption of water vapor with a heat effect approaching that of the heat of vaporization of water and a section of the isotherm which is concave upward at high relative humidity.

Thus, the adsorption of water by cellulose fibers at low relative humidities can be described in terms of a specific surface adsorption of the Langmuir[23] type, and at high relative humidities in terms of multilayer or polymer–liquid solution theory. This treatment adequately describes most sorption phenomena, especially if it is noted that the two primary processes occur simultaneously and inseparably. Some "multilayer" formation or polymer–liquid mixing undoubtedly occurs even at very low humidities. The amount of water and polymer involved in this process increases gradually with increasing relative humidity and becomes predominant at high water vapor pressures. At these high vapor pressures the overall sorption process is intermediate between the two extremes of adsorption on preferred sites and of random mixing of polymer and liquid.[10] Conversely, adsorption of water by hydrogen bond formation on preferred sites predominates at low vapor pressures and, although the amount of sorbed water involved gradually increases with increasing relative humidity, its contribution to the total sorption diminishes at high vapor pressures. It has not been possible to evaluate the exact contribution of each process to the total sorption at any given relative humidity. Calorimetric studies of freezing and nonfreezing water by Magne, Portas, and Wakeham[24] do, however, support the above mechanism. On the basis of the assumption that water adsorbed by hydrogen bonding will not freeze, these workers found that in viscose rayon at −13.6°C. practically all the first 25% water adsorbed was nonfreezing and that with increasing water content the nonfreezing water reached a maximum value of about 31%. For Rowden cotton at −12.8°C. all the water up to 6.4% was of the nonfreezing type, and the maximum value with increasing water content was about 14% water. On the basis of these figures all water adsorbed by viscose rayon up to 25% would be bound water, from 25 to 35% water both bound and free water are added, and all additional water above 35% would be added as water dissolved in the cellulose or as capillary water. Because of assumptions necessary for interpretation, these data constitute only a first approximation.

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[23] I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).

More recently, Preston and Nimkar[25] studied freezing-point lowering and solubility curves for cellulose fibers and concluded that the behavior agreed with the solution hypotheses. For viscose rayon fibers, breaks in the cooling curve were observed, and with decreasing water content between 50 and 37.5% the freezing point of the water decreased. A plot of the temperature of the cooling curve inflection versus the concentration of water in the fiber yields a curve similar to the freezing-point lowering curve for a binary system. To produce a given freezing-point lowering, the water content in viscose rayon must be twice as great as that in cotton. According to the solution hypothesis this can be readily explained by the fact that there is approximately twice as much noncrystalline cellulose in viscose rayon as in cotton and, therefore, that it requires twice as much water to produce the same solution concentration in rayon as in cotton.[25]

Conclusive proof that sorption by cellulose is a dual process comprised of overlapping surface sorption and solution processes cannot be offered, but it seems to be plausible for unmodified celluloses and water vapor. It is

[24] F. C. Magne, H. J. Portas, and H. Wakeham, *J. Am. Chem. Soc.*, **69**, 1896 (1947).

[25] J. M. Preston and M. V. Nimkar, *Textile Research J.*, **23**, 119 (1953).

not necessary that the mechanism for cellulose be general for all other polymers because in other cases the mechanism may vary with chemical composition of the fiber. In nylon fibers, for example, the moisture sorption has been interpreted as occurring from the attachment of one water molecule to each free carboxyl and imido group.[26] This primary adsorbed water accounts for most of the water adsorbed by nylon up to 90 to 95% relative humidity. Because of the hydrocarbon nature of the nylon monomers, very little adsorption by a solution process would be expected and all additional water must be adsorbed as multilayers or as capillary condensed water.[24] Similarly, the solution process as a factor in moisture sorption is less pronounced as the hydrophobic nature of cellulose is increased by esterification to form such compounds as the tributyrate or tristearate. In these cases the total moisture sorption decreases and the rapid rise in sorption at high relative humidity does not occur. Thus, the solution process during sorption becomes a major factor only when the sorbate is a swelling agent or solvent for the polymer in question. Cellulose trinitrate, for example, has very little affinity for water, but shows marked sorption of a solvent, acetone, primarily by a solution process and actually dissolves at high acetone vapor pressures.[10] The most probable mechanism of sorption must therefore be chosen from consideration of the polymer, the sorbate, and polymer–sorbate interaction. In all cases studied the mechanism may be either sorption on specific sorption sites, multilayer formation, capillary condensation, solution processes, or combinations of two or more of these factors.

For cellulose itself, two other mechanisms of sorption are still prevalent. These are sorption by (1) hydrate formation and (2) capillary condensation.

(1) Hydrate Formation by Cellulose

After mercerization of cellulose was discovered, the hypothesis that the product after mercerization differed from the original sample only in that it contained water bound in its structure was widely accepted, and mercerized cellulose was commonly known as "cellulose hydrate" or hydrate cellulose. Since that time many investigators have proposed formulas for cellulose hydrates while others deny the existence of stoichiometric cellulose–water compounds. At this time, no general agreement has been reached. In all cases, the question centers about whether or not that portion of the water present as "bound" water in a cellulose sample actually represents a specific compound.

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[26] L. Pauling, *J. Am. Chem. Soc.*, **67**, 555 (1945).

Among a number of ways in which water in a swollen fiber, bound by specific interaction with cellulose, shows its reduced activity is a reduction in solvent power for a third water-soluble component. The swelling water in cellulose, in equilibrium with an aqueous salt solution, contains less of the solute than does the surrounding water. Since the exact status of each molecule of the swelling water is unknown, it is customary to assume that part of the water dissolves no solute at all while the remainder of the water acts as if it were free. This leads to the postulation of a certain amount of "nonsolvent" water in cellulose fibers. Champetier[27] determined this nonsolvent water by soaking cellulose fibers in aqueous solutions of a reference substance, such as sodium thiosulfate or pyridine, pressing out the solution, and determining the reference substance. In all cases, the concentration of reference substance was found to be higher than the original concentration and independent of the pressures used. Champetier found that native fibers contained about 0.50 mole of nonsolvent water per anhydroglucose unit while mercerized fibers contained about 1.0 mole nonsolvent water. Tankard[28] modified Champetier's method by employing higher pressures and confirmed Champetier's results. Tankard's results are given in Table 16. Similar results have been obtained by other workers.[29-31]

Champetier tried to express the ratios between cellulose and nonsolvent water in terms of stoichiometric hydrates. This leads to the existence of two hydrates, $(C_6H_{10}O_5)_2.H_2O$ and $C_6H_{10}O_5.H_2O$. Tankard, however, interpreted his results as representing the maximum amount of water which may be regarded as chemically combined rather than as demonstrating the existence of definite stoichiometric cellulose hydrate. The latter view is most plausible on the basis of x-ray results which indicate that for the most part water does not penetrate the interior of the crystalline regions and, therefore, that a uniform hydrate composition cannot exist throughout the whole fiber.

Sakurada and Hutino[32] have shown that when a swelling compound, such

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[27] G. Champetier, *Compt. rend.*, **192**, 1593 (1931); **195**, 280 (1932).

[28] J. Tankard, *J. Textile Inst.*, **28**, T263 (1937).

[29] E. Heymann and G. C. McKillop, *J. Phys. Chem.*, **45**, 195 (1941).

[30] A. M. Sookne and M. Harris, *Textile Research*, **10**, 405 (1940).

[31] P. H. Hermans, *Contributions to the Physics of Cellulose Fibres*, Elsevier, New York, 1946, pp. 103–106.

[32] I. Sakurada and K. Hutino, *Kolloid-Z.*, **77**, 346 (1936).

TABLE 16

Nonsolvent Water in Cellulose and Cellulose Derivatives (Tankard[28])

Material	Moles nonsolvent water per mole $C_6H_{10}O_5$
Cotton	0.49
Mercerized cotton	0.75
Mercerized cotton before drying	0.99
Linen	0.55
Mercerized linen	1.05
Viscose rayon	0.97
Mercerized viscose rayon	1.17
Lilienfeld rayon	1.10
Acetate rayon	2.30
Cellulose monomethylene ether	3.03
Hydrocellulose	0.67

as alkali cellulose, is washed with water and then examined while still wet, it gives a characteristic x-ray diagram. This diagram indicates that the sodium hydroxide of the alkali cellulose has been displaced by water which now occupies a definite position in the crystal lattice. This swollen modification was said to represent a true hydrate of cellulose and was called "water cellulose." This compound is very unstable and loses water slowly when stored in water at low temperatures and rapidly when either heated in water or dried. Hermans and Weidinger[33] investigated more fully and described two hydrates of cellulose. One of these hydrates, called cellulose hydrate II, was identical with water cellulose and cannot be formed from cellulose and water, but only by washing swelling compounds with water. Its probable composition, calculated by the method of Sakurada and Okamura,[34] was given as $C_6H_{10}O_5 . 1^1/_3H_2O$ or $C_6H_{10}O_5 . 1^1/_2H_2O$. When cellulose hydrate II is heated in water it is transformed into a hydrate of lower water content called cellulose hydrate I. The probable composition of this hydrate was given as $C_6H_{10}O_5 . ^1/_3H_2O$ or $C_6H_{10}O_5 . ^1/_2H_2O$. From x-ray evidence, this hydrate was shown to be formed on sorption of water by regenerated cellulose, and its formation was complete at 65% relative humidity In contrast, cellulose hydrate I is not formed by crystalline regions of native cellulose fibers. More recently, Legrand[35] with Champetier[36] investigated the hydration of cellulose by x-ray diffraction. From variations in intensity and line position on the x-ray diagrams of wet cellulose fibers, these authors conclude that the crystal lattice of all forms of cellulose are acessible to water. The crystal lattice of native cellulose fibers was found to be less affected by water sorption than the lattice of regenerated cellulose fibers. These authors also question the composition of the various hydrates given by Hermans and state that x-ray diffraction does not allow the determination of stoichiometric ratios.

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[33] P. H. Hermans and A. Weidinger, *J. Colloid Sci.*, **1**, 185 (1946).

[34] I. Sakurada and S. Okamura, *Kolloid-Z.*, **81**, 199 (1937).

[35] C. Legrand, *Bull. Soc. Chim. Belges*, **57**, 113 (1948).

[36] S. Champetier and C. Legrand, *J. Polymer Sci.*, **10**, 223 (1953).

According to Hermans,[37] the first concave portion of the sorption isotherm corresponds to the formation of cellulose hydrate I in the amorphous part of native cellulose fibers and in both the amorphous and crystalline parts of regenerated cellulose fibers. The next straight-line portion of the isotherm would then correspond to the formation of cellulose hydrate II in the amorphous part of both native and regenerated celluloses. The last rapidly rising portion of the isotherm arises from water bound by weaker forces of multilayers or capillary condensation. This hypothesis requires the coexistence of hydrates of varying composition at a given relative humidity. Hailwood and Horrobin[11] obtained good agreement between calculated and observed values for moisture sorption by cellulose by assuming the formation of a monohydrate of cellulose. In view of the assumption made by these authors that the heat of mixing is zero, this agreement must be regarded as fortuitous rather than as evidence of hydrate formation.[12]

Basically, the hydrate mechanism for sorption is identical with the general mechanism discussed above, except for the assignment of definite compositions to the hydrates. Actually the evidence for true hydrate formation is not conclusive and is based on the tenet that x-ray diagrams show that water swells regenerated cellulose intramicellarly and, hence, that true hydrates must be formed. This definite conclusion is questionable in that although the change in x-ray does prove that the packing is changed by water addition, it does not necessarily prove a constant invariable composition of the "hydrate." It is now recognized that variations in composition may occur in polymeric systems without appreciable variation in molecular packing. It is also difficult to demonstrate geometrically how a water molecule adsorbed by hydrogen bonding can be shared by 2 or 3 anhydroglucose units in such a way that the 101 distance is increased by only 0.5 A. as reported for cellulose hydrate I. In addition, the increase in the 101 distance occurs gradually with increasing regain for cellulose hydrate I formation; the decrease in 101 distance also occurs gradually as cellulose hydrate II is decomposed. It appears to the author that such changes in x-ray diagram can be more closely associated to solution and swelling phenomena based on kinetic equilibria rather than to the coexistence of a number of true hydrates. The actual formation of true hydrates in amorphous regions of cellulose fibers has not been directly demonstrated.

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[37] P. H. Hermans, *Physics and Chemistry of Cellulose Fibres*, Elsevier, New York, 1949, p. 189.

It is the opinion of the author that the overwhelming mass of evidence favors a mechanism of sorption based on kinetic sorption on preferred sites rather than a formation of stoichiometric hydrates. There seems no doubt that hydration by hydrogen bond interaction between water and cellulose does occur. The prediction of stoichiometric hydrates of cellulose, however, is of doubtful significance and the use of cellulose hydrate terminology is somewhat confusing and limited in application.

(2) Capillary Condensation

One of the earliest theories for the adsorption of vapors by solids was the capillary condensation theory. This theory is based on the fact that the vapor pressure of water in a capillary depends on the radius of the capillary. The vapor pressure decreases with decreasing capillary radius. The capillary theory will satisfactorily account for sorption phenomena including hysteresis for rigid nonswelling solids,[38] but it seems untenable for sorption of polar molecules on cellulose fibers.

Several objections to this theory have been offered. In the first place, it is doubtful that the capillary theory as expressed by the Kelvin equation is valid in pores whose diameter is too close to the molecular radius of the sorbate. In fact, Cohan[38] concludes that even for rigid gels the capillary theory can be applied only if it is assumed that a monomolecular layer of sorbate is formed before capillary condensation begins. It is doubtful, therefore, that any capillary condensation of water in the usual sense would occur below about 40% relative humidity. The capillary theory would also require that, at relative vapor pressures of sorbates equivalent to equal values of capillary radius in the Kelvin equation, the volume of liquid adsorbed should be the same for all sorbates and independent of temperature. Cohan,[38] however, states that the volumes adsorbed need to be constant only if the monomolecular layer adsorption is negligible compared to capillary condensation. Even so, it is difficult to reconcile the great specificity of sorption by cellulose with a physical condensation process. For example, the very great adsorption of water and very small adsorption of benzene at the same relative vapor pressure of each sorbate[39] indicate strongly that capillary condensation as such is not a major factor in the sorption process for cellulose fibers.

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[38] L. H. Cohan, *J. Am. Chem. Soc.*, 66, 98 (1944).

The most serious objections to capillary condensations as a sorption mechanism lie in that fact that (1) most fibers, especially those of regenerated cellulose, do not have any permanent capillary space, and (2) the capillary theory offers no explanation for the swelling which accompanies vapor sorption. Hermans[40] prepared experimental regenerated fibers and found that the density, as measured directly by volume measurements made microscopically and as measured by flotation in organic liquids, agree within experimental accuracy. From these experiments he concluded that regenerated cellulose fibers do not contain capillary systems. Similarly from microscopic measurement of the volume of the cell walls of ramie[41] and the density in benzene, Hermans concluded that ramie may contain as much as 10% pore volume. Any water condensing in such a capillary system should produce a slight shrinkage of the fiber because of the surface forces of the water in the capillary. It is a well-established fact[40,42,43] that as a first approximation every water molecule adsorbed by cellulose contributes its molecular volume to swelling. At high relative humidities greater than 0.7 where capillary condensation is assumed to take place, the increase in volume of the fiber is exactly equal to the volume of water absorbed. According to Preston and Nimkar[25] the amount of capillary water which does not contribute to swelling cellulose fibers is significant only above 99% relative humidity.

Capillary condensed water in the usual sense does not, therefore, seem to be a major factor in sorption phenomena, but it does play an important role in textile application of fibers. For example, all cellulose fibers after immersion in water will hold much more water than is indicated by sorption isotherms at 100% relative humidity. Properly treated cotton fibers may hold as much as 300% water and most viscose rayon fibers between 150 and 250%. Not more than 35% of this water for cotton and 60–80% for rayon contributes to the volume swelling of the fibers. The remainder is held by capillary forces in the usual sense. The amount of capillary water held by a particular fiber is more closely related to such macroscopic factors as the presence or absence of a lumen, the nature of the fiber surface, the shape of the cross section, the filament size, the filament size uniformity, and the distribution of fiber length than to submicroscopic structure factors. Thus, cotton, with a lumen, irregular shape, and nonuniform filament diameter, holds larger amounts of capillary water than most viscose rayons and finds wide use in applications where liquid absorption is important.

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[39] K. Lauer, *Kolloid-Z.*, **107**, 86 (1944).

[40] P. H. Hermans, *Contributions to the Physics of Cellulose Fibres*, Elsevier, New York, 1946, Chapter IV.

[41] A. Frey-Wyssling and H. Speich, *Helv. Chim. Acta*, **25**, 1474 (1942).

[42] G. E. Collins, *J. Textile Inst.*, **21**, T311 (1930).

[43] P. H. Hermans, D. Vermaas, and J. J. Hermans, *J. makromol. Chem.*, **1**, 247 (1944).

(c) TEMPERATURE DEPENDENCE OF SORPTION

The most extensive study of the effect of temperature on sorption was made by Wiegerink[44] who determined both adsorption and desorption values for ten different fibers including raw, purified, and mercerized cotton and viscose, cuprammonium, and acetate rayons between 35.5° and 150°C. The results for kier-boiled cotton are given in Figure 64. Complete iso-

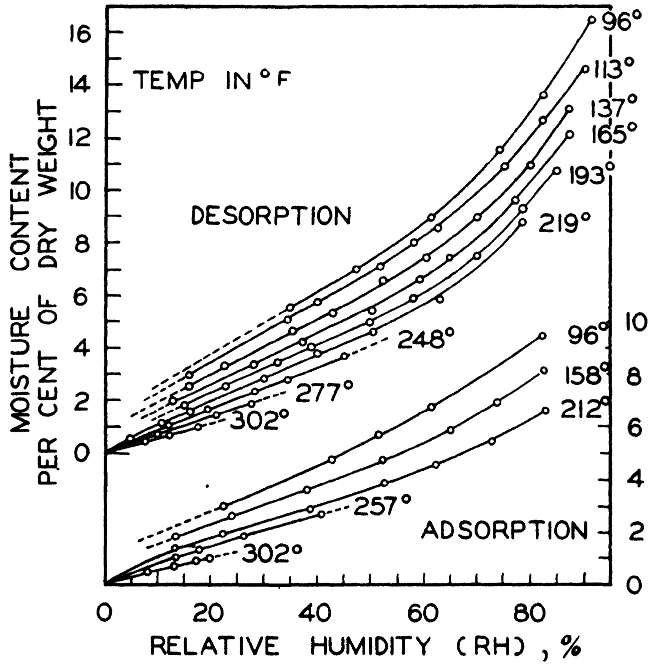

Fig. 64. Sorption isotherms of purified cotton at various temperatures (Wiegerink[44]).

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[44] J. G. Wiegerink, *J. Research Natl. Bur. Standards*, **24**, 645 (1940).

therms are not given in all cases, for above 100°C. the relative humidity was restricted to the range in which the vapor pressure of water was less than one atmosphere. The equilibrium water content decreases steadily with increasing temperature for both adsorption and desorption. The reduction in moisture content for a given temperature difference decreases steadily at high temperatures. Wiegerink established that up to 212°F.

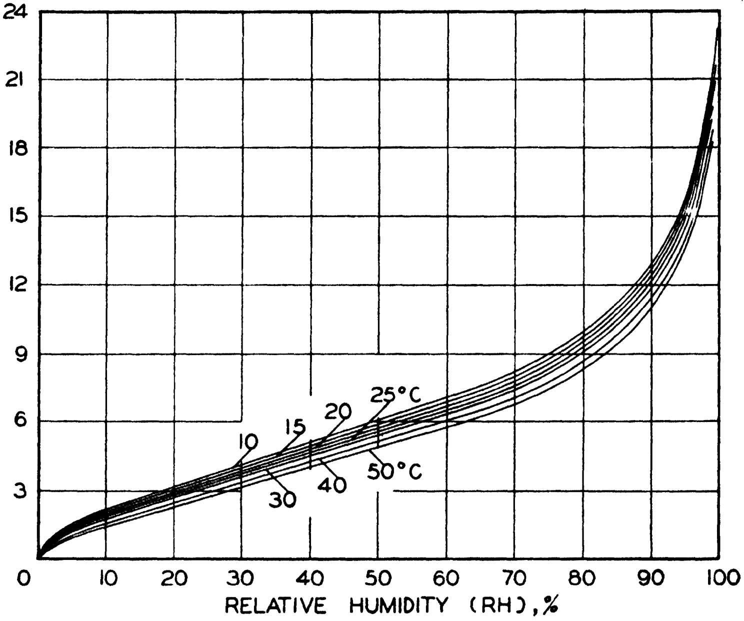

Fig. 65. Adsorption isotherms of kier-boiled cotton at low temperatures (Urquhart and Williams[45]). Ordinate, per cent moisture regain.

at constant relative humidity there is a linear relation between the logarithm of moisture content and the reciprocal of the absolute temperature. The results for all other materials studied were quite similar to those given in Figure 64 except for the magnitude of the sorption.

Urquhart and Williams[45] made an extensive study of the influence of temperature between 10° and 110°C. on the sorption of water by cotton fibers. They found that for a constant relative humidity below about 85% the moisture content decreased regularly with increasing temperature only for the range from 10° to 50°C. Between 60° and 110°C. an increase in temperature produced an increase in moisture content. These relations are shown in Figures 65 and 66. According to Urquhart and Williams[45] the increased sorption at high temperature and humidity arises from the fact that thermal effects break cellulose–cellulose hydrogen bonds and free a greater number of hydroxyl groups for sorption.

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[45] A. R. Urquhart and A. M. Williams, *J. Textile Inst.*, **15**, T559 (1924).

Limited studies for the effect of temperature on sorption by other materials have been made by a number of investigators. Newsome and Sheppard[46] investigated the temperature dependence of sorption of cellulose acetate films (39% acetyl) between 30° and 50°C. Simril and Smith[47] worked with cellophane between 16.5° and 49.5°C. The moisture content at a given relative humidity decreased with increasing temperature throughout the entire humidity range for both these materials. Stamm and Loughborough[48] studied the drying of Sitka spruce at temperatures ranging from 25° to 100°C. They found that increasing temperature decreased the equilibrium moisture content for all relative humidity values The crossing of the sorption isotherms found for cotton was not found in

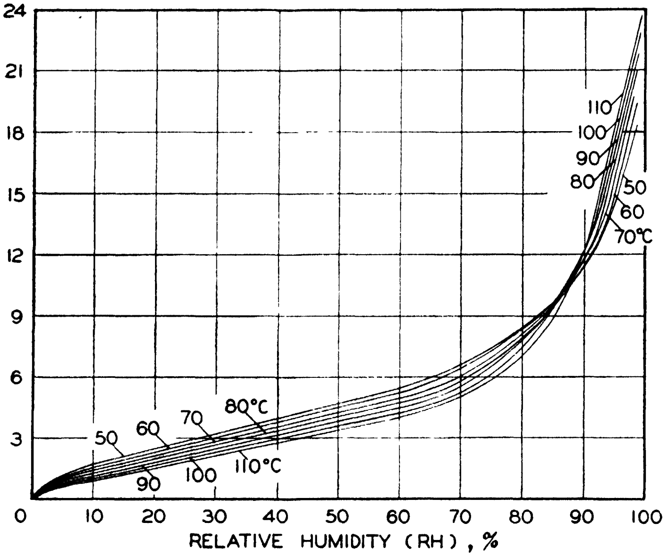

Fig. 66. Adsorption isotherms of kier-boiled cotton at high temperatures (Urquhart and Williams[45]). Ordinate, per cent moisture regain.

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[46] P. T. Newsome and S. E. Sheppard, *J. Phys. Chem.*, **36**, 930 (1932).

[47] V. Simril and S. E. Smith, *Ind. Eng. Chem.*, **34**, 226 (1942).

[48] A. J. Stamm and W. K. Loughborough, *J. Phys. Chem.*, **39**, 121 (1934).

this case. These authors[48] point out that such behavior would not be expected in desorption from the green condition because before the initial drying of wood a maximum number of the hydroxyl groups in the cellulose are adsorbing water and, therefore, their number could not increase at higher temperatures. This effect should be general for all green fibers including cottonfrom the boll and freshly spun viscose rayon.

Very few data on sorption of water at low temperatures are available, but Darling and Belding[49] have studied sorption by cotton, viscose rayon, and acetate rayon at 40°, 0°, and −20°F. They conclude that at constant relative humidity, relative to saturation over water, the equilibrium adsorption moisture content for these fibers is about the same at 40°F. and 0°F. but somewhat lower at −20°F. This conclusion implies that cellulose fibers have a maximum moisture adsorption between 40° and 0°F. They also report that the linear relation between the logarithm of moisture content and 1/T reported by Wiegerink[44] does not hold over the entire range between −20° and +160°F. The curve flattens between 40° and 0°F., and the slope reverses at lower temperatures. These findings have been criticized as improbable by Whitwell and Toner[50] who suggest that the decrease in sorption at low temperature may be related to the blocking of sorptive surfaces by ice crystal formation. Such a decrease at low temperature could arise, however, from a decrease in the mobility of the molecular network at low temperature and hence a decrease in the ability of water to swell the fiber at low temperatures. Apparently, more intensive investigations are needed before a definite interpretation can be offered for sorption at low temperatures.

(d) PERMEABILITY AND DIFFUSION

The study of permeability and diffusion of gases and vapors through films of cellulose and cellulose derivatives can be used to study the interaction of water with the film and the nature of the films themselves. The results obtained from films should be generally applicable to regenerated fibers of either cellulose or cellulose derivatives. Exact application of film results to native fibers would not be expected because of possible effects on porosity of gross structural features such as surface cracks and lumen which are not present in films.

In general, there are two concepts of permeability. Gas or vapor can either pass through capillary openings or the gas or vapor molecules can dissolve in the film and diffuse through it as a gas through a liquid. For

[49] R. C. Darling and H. S. Belding, *Ind. Eng. Chem.*, **38**, 524 (1946).

[50] J. C. Whitwell and R. K. Toner, *Ind. Eng. Chem.*, **38**, 1203 (1946).

films of organic high polymers, most experimental data support the solution mechanism. In the simplest case, the steady state permeability of film to a gas can be set equal to the product of the diffusion constant for the gas in the film and the solubility coefficient of the gas in the film. This relation depends upon the assumption that both Fick's law of diffusion and Henry's law apply. It has been verified for a number of permanent gases by Barrer[51] and reported to hold for water vapor in a number of polymers by Doty, Aiken, and Mark.[52] More recent work of Hauser and McLaren[53] has shown that, for water vapor, this relation is valid for vinyl polymers at low relative humidity but that its use is questionable in reference to cellulose, cellulose derivatives, and other materials with a high affinity for water vapor. For these materials, the diffusion constant is a function of water content, and Henry's law is not obeyed. No general relation is known for these substances.

As a general rule, cellulose derivatives are more permeable to dry permanent gases than cellulose, but both materials are among the least permeable of organic film-forming materials. According to de Boer and Fast,[54] a film of cellulose triacetate, 25 microns thick, passed 76.0 mm.^{3} per cm.^{2} per hour of hydrogen, and a regenerated cellulose film, 7 microns thick, passed only 0.95 mm.^{3} per cm.^{2} per hour. Similar data were obtained for cellulose nitrate. Low permeability to dry gases is apparently general for materials rich in hydroxyl groups. Dry regenerated cellulose films are also impermeable to dry air.[54,55] Trillat and Matricon[55] found, however, that diffusion of air increased sharply with increasing moisture content. By passing moist air through a dry membrane and dry air through a moist membrane the action of moisture was found to be reversible.

As expected, the permeability of both cellulose and cellulose-derivative films to water is quite high. Exact comparison of different materials is frequently not possible because of wide variations in experimental procedure used for different materials. As a first approximation, however, it seems that the permeability increases with increasing hydrophilic nature of the material. The permeability usually increases with increasing moisture content of the film, but again an exact permeability grouping is not possible. For example, cellulose acetate films may be much more permeable than regenerated cellulose at low relative humidity, but at high relative humidity the permeability is about the same for both materials.[53] Apparently, the permeability to a given vapor is a function both of the sorption capacity of the material for the vapor and the structure of the film.

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[51] R. M. Barrer, *Diffusion in and through Solids*, Macmillan, New York, 1941.

[52] P. M. Doty, W. H. Aiken, and H. Mark, *Ind. Eng. Chem., Anal. Ed.*, **16**, 686 (1944); *Ind. Eng. Chem.*, **38**, 788 (1946).

[53] P. M. Hauser and A. D. McLaren, *Ind. Eng. Chem.*, **40**, 112 (1948).

[54] J. H. de Boer and J. D. Fast, *Rec. trav. chim.*, **57**, 317 (1938).

[55] J. J. Trillat and M. Matricon, *J. Chim. Phys.*, **32**, 101 (1935).

Using model regenerated cellulose filaments, Hermans and Vermaas[56] have shown that the conditioning of dry cellulose filaments follows a heterogeneous course. By microscopic examination, they found that the adsorption of moisture could be followed by a boundary line which moves gradually to the center of the fiber. Apparently, the outer part of the filament reaches equilibrium regain quickly while the inner part inside the boundary line remains dry. Their experiments demonstrate that at low relative humidity the velocity of diffusion of water through dry cellulose is very slow and takes place with difficulty. At higher regains, enhanced swelling of the fibers by higher water sorption allows faster diffusion; as a first approximation, the velocity of diffusion increases exponentially with increasing relative humidity. Similar experiments showed that glycerol will not diffuse at all into dry fibers, but that rapid diffusion of glycerol will take place if the fiber is preswollen with a certain amount of water. Glycerol diffusion does not occur to any extent below 65% relative humidity and increases rapidly at higher relative humidities. Thus, water added over that portion of the isotherm for which most water is bound does not aid diffusion whereas water added as solution water increases it greatly. From all these results it seems reasonable that changes in diffusion of a second material into cellulose as a function of the water content of the fiber are related to the swelling of the fiber and the solubility of the second material in water. This phenomenon should be general for other swelling reagents for cellulose and cellulose derivatives.

The physical picture from this evidence can be summarized in the following manner. Dry cellulose films or fibers consist of dense, nonporous networks which do not dissolve permanent gases to any extent and are impermeable to liquids or vapors which do not interact with and swell cellulose. Water or other swelling reagents increase the solubility of the gases or vapors in the network system and also swell the network to allow more rapid diffusion. This more rapid diffusion in swollen networks is associated with the plasticizing action of the water or swelling reagent. The lower attractive forces between chains result in more rapid Brownian motion of segments of the chains and therefore more rapid diffusion. This plasticizing action is also associated with the greater flexibility and softness of swollen fibers. A material which alone will not penetrate dry cellulose can be mixed into the system by preswelling with a swelling reagent for cellulose in which the nonswelling reagent is soluble. These principles have their best demonstration in the mechanisms ascribed to various cellulose esterifications and etherifications (see Chapter IX).

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[56] P. H. Hermans and D. Vermaas, *J. Polymer Sci.*, 1, 149 (1946).

(e) THERMODYNAMICS OF SORPTION

As pointed out in the previous discussion, adsorption on a swelling polymer is analogous in many ways to solution in a liquid. It is possible to apply a thermodynamic treatment to sorption and swelling which is essentially identical with that applied to dilute solutions. This treatment has been presented in excellent reviews.[2,57] The discussion here will be limited to a brief discussion of various thermodynamic quantities and their relations to cellulose structure and the mechanism of sorption. An excellent review of thermodynamic data for various cellulose fibers has been given by Rees.[58]

The adsorption of vapors by a solid adsorbent is usually accompanied by the evolution of heat. In the case of adsorption of moisture, the amount of heat evolved depends upon (1) the nature of the adsorbing material, (2) the amount of water adsorbed, and (3) whether the water is adsorbed from the liquid or vapor state. The expression of evolved heat is of most general interest in the form of heats of wetting or the differential heat of sorption. The heat of wetting is defined as the heat evolved when the material at any given moisture regain is completely wetted. It is usually expressed as calories per gram of the dry material. The differential heat of sorption at a given moisture regain α is defined as heat evolved when 1 gram of water is adsorbed by an infinitely large mass of material at regain α. The heat of adsorption from the vapor phase will be greater than that from the liquid phase by an amount equal to the heat of condensation of water. For convenience, all heat values used here will refer to liquid water and the heat of adsorption will be expressed as calories per gram of water adsorbed.

The differential heat of adsorption is a measure of the energy required to break the adsorbed water away from the adsorbent. It has its greatest value at zero moisture regain, and decreases rapidly with increasing moisture content. The differential heat of sorption at zero regain is essentially the same for all cellulosic materials. Its most probable value lies between 280 and 300 calories per gram of water adsorbed.[58,59] These values cor-

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[57] R. L. Steinberger, *Textile Research*, **4**, 451, 513 (1933).

[58] W. H. Rees, *J. Textile Inst.*, **39**, T351 (1948).

[59] J. C. Guthrie, *J. Textile Inst.*, **40**, T489 (1949).

respond to 5.0 to 5.4 kcal. per mole of water. These data indicate that the nature of the sorption process is identical for all types of cellulose and that the initial water adsorbed is held by hydrogen bond formation with cellulose hydroxyls.

The heat of wetting, on the other hand, varies considerably with the origin of the cellulose as indicated by the data of Rees[58] in Table 17. The heat of wetting depends upon the accessibility of the hydroxyl groups in any particular sample; as a first approximation, it is directly proportional to the amount of amorphous cellulose present in the sample. The heat of wetting may be used as a measure of the proportion of amorphous material present. Since the heat of wetting is almost exactly proportional to the moisture regain, however, most measurements of amorphous content are made by the simpler regain method.

TABLE 17

Integral Heats of Wetting of Cellulose Fibers (Rees[58])

Material	Heat of wetting (cal./g.)	Moisture regain[a]
Cotton	11.0	
Cotton, mercerized under tension	17.5	
Cotton, mercerized relaxed	18.4	
Fortisan	18.2	11.7
Viscose rayons		
Durafil	20.4	13.5
Tenasco	22.9	14.2
Viscose ("A quality")	25.2	24.7

[a] Determined at 65% R.H. and 25°C.

The dependence of the heat of wetting on the moisture content of the sample are shown by the data of Rees[58] in Figure 67. These data, like differential heat of sorption values derived from them, show that the first quantities of water are bound with a very large heat effect and that at higher water content the heat effect decreases rapidly and approaches zero asymptotically. This change in heat effect can arise from two sources: (1) the water added at high water content is adsorbed by weaker forces than those operating at low water content; and (2) the heat effect observed is the sum of the heat evolved on sorption of water molecules and the heat adsorbed by the breaking of secondary bonds between cellulose molecules as the fiber swells. As outlined in the previous discussion of mechanism of water sorption, both these factors contribute to diminished heat of sorption at higher moisture content. Quantitative evaluation of the importance of each factor at various moisture levels has not been possible.

Stamm and Loughborough[48] and Guthrie[59] have determined differential heat of sorption and free energy changes during sorption for a number of fibers. These investigators found that in early stages of adsorption the free energy change is smaller than the heat change; hence, there is a decrease in entropy when one gram of water is added to an infinitely large sample. The $T\Delta S$ value at zero moisture content is approximately equal to the latent heat of fusion of water. This implies that the first adsorbed water has a degree of orientation and association comparable to that of ice. At saturation the free energy approaches zero and therefore the entropy change will be very small. Thus, the water adsorbed near saturation is very similar to liquid water.

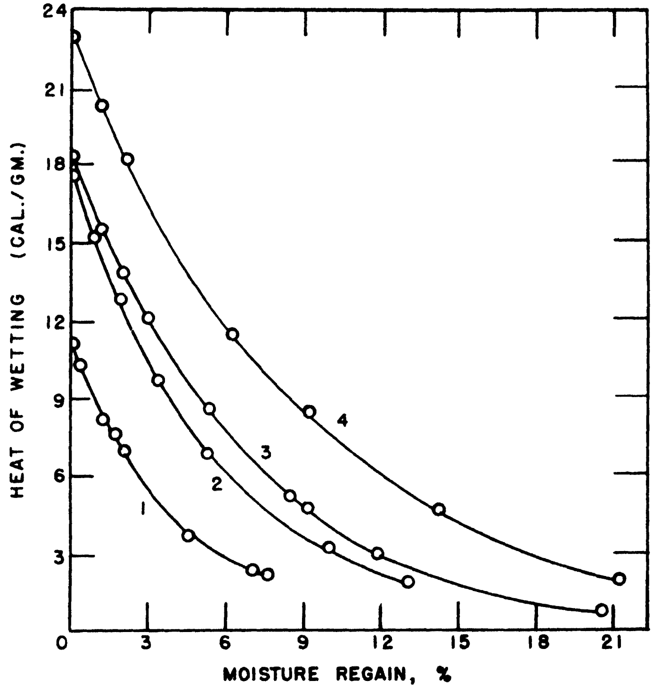

Fig. 67. Heat of wetting of cellulose fibers as a function of moisture regain (Rees[58]) curves: (1) cotton; (2) cotton mercerized under tension; (3) Fortisan; (4) Tenasco viscose rayon.

Sheppard and Newsome[46] and Guthrie[59] found that the differential heat of sorption at zero moisture content for secondary cellulose acetate was approximately the same as that found for cellulose. The mechanism of sorption is, therefore, probably the same for the two fibers. This may be regarded as general for partial cellulose esters and for triesters which are capable of hydrogen bond formation. Similarly, Thomas[60] found that at low water content the entropy change of sorption of water by cellulose acetate approached that of the entropy change on changing water to ice.

2. Cellulose Structure–Sorption Phenomena

(a) HYSTERESIS

It has long been known that one of the characteristics of sorption isotherms is a sensitive dependence upon the previous sorption and drying history of the sample. For a given fiber sample the moisture regain at a given relative humidity is greater when the fiber is brought to equilibrium from the wet state or a higher relative humidity than when the fiber is brought to equilibrium from the dry state or a lower relative humidity. This phenomenon is general for cellulose and cellulose derivatives and is known as hysteresis. The hysteresis effects which have been observed for cellulose fibers are shown schematically in Figure 68 which is patterned from the results of Urquhart and Eckersall.[61]

If moist cotton fibers are taken directly from the boll and without further drying are brought to equilibrium in atmospheres of successively lower relative humidity, the desorption follows a course similar to that in curve 1 in Figure 68. If these dry fibers are now brought to equilibrium in atmospheres of successively increasing relative humidity, the resulting adsorption will follow a course similar to curve 2 in Figure 68. This is the standard adsorption isotherm. If the fibers are again brought to equilibrium at successively lower relative humidities, the desorption follows curve 3 which is a standard desorption isotherm. Once adsorption history has been established, repeated adsorption and desorption over this same cycle will give the same hysteresis loop bounded by curves 2 and 3. Equilibrium of the fiber with water vapor may be established at any point within this loop under suitable conditions. For example, partial adsorption to point A in Figure 68 followed by desorption will give an equilibrium desorption curve similar to the dotted line AB. Similarly, partial desorption to point C followed by adsorption will give an equilibrium adsorption curve similar to CD. Urquhart and Eckersall also found that above 80% relative humidity the desorption curve started from a water-soaked sample is higher than the curve from a sample in equilibrium with a saturated atmosphere down to about 80% relative humidity. Below this point the two curves coincided.

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[60] A. M. Thomas, *J. Appl. Chem. (London)*, **1**, 141 (1951).

[61] A. R. Urquhart and N. Eckersall, *J. Textile Inst.*, **21**, T499 (1930).

Thus, the primary desorption of moist cotton is irreversible and the primary desorption curve lies above the standard desorption isotherm over

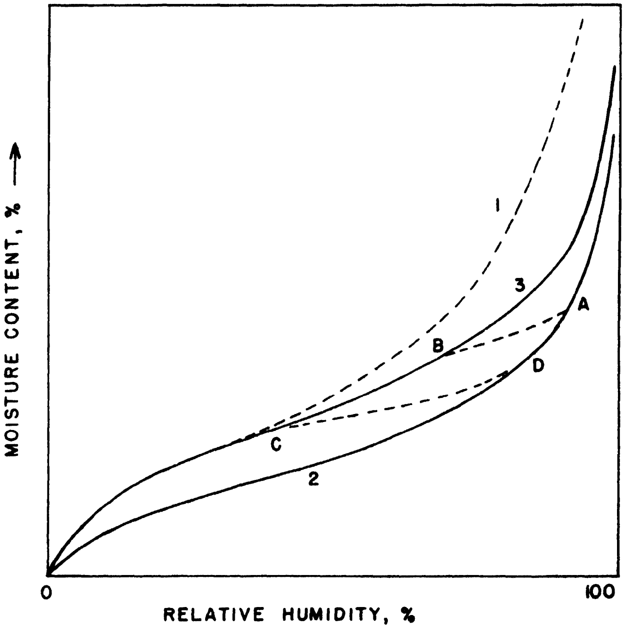

Fig. 68. Hysteresis effects in sorption of water vapor by cellulose fibers (schematic). Curves: (1) desorption by fresh fibers on first drying; (2) adsorption; and (3) desorption isotherms by fibers after first drying. AB represents the course followed on desorption after partial adsorption; CD represents the course of adsorption after partial desorption. The per cent moisture content is on dry-weight basis.

the whole range of relative humidity. This effect is general for all fibers taken directly from a highly swollen state such as undried native fibers or wood, undried mercerized fibers, and regenerated fibers on the first drying after spinning. The exact shape and position of this primary desorption will depend to some extent on particular conditions of growth or processing of natural fibers and of manufacture in regenerated fibers. Once a sorption history has been established by drying the fibers, the adsorption–desorption behavior of most cellulose fibers regardless of origin is quite similar even though the total sorption at a given humidity may vary widely for different fibers. Seborg[62] showed that the ratio of the adsorption to the desorption regain was essentially constant at all relative humidities except at the ends of the hysteresis loops. The adsorption–desorption ratio varies only slightly for different fibers and is usually between 0.80 and 0.90 for both native regenerated fibers and cellulose acetate at room temperature. Hysteresis effects decrease with increasing temperature and become very small in the vicinity of 100°C., where the adsorption–desorption ratio approaches unity.[45]

As previously pointed out, a satisfactory explanation for hysteresis effects for rigid nonswelling gels may be made on the basis of the capillary condensation theory. This explanation, however, is not applicable to substances capable of swelling such as textile fibers. For fibers, the most probable source of hysteresis is that proposed by Urquhart[18] and restated in modern form by Smith[15] and White and Eyring.[7]

Let a completely dry cellulose fiber composed of a molecular network structure (as discussed in Section B of this chapter) be allowed to come to equilibrium with atmospheres of increasing relative humidity. Molecules of water are adsorbed and cause swelling of the network. The swelling breaks secondary bonds between the molecules of the network and causes the number of hydroxyl groups capable of acting as strong sorption sites to increase with increasing relative humidity. If desorption is now allowed to occur, the network tends to contract. The collapse of the network is delayed, however, by the persistence of bound water on the new sorption centers formed on adsorption. Therefore, a higher regain occurs at a given relative humidity on desorption. Actually, the sorbed water molecules either in the bound or normally condensed phases are in equilibrium with water vapor at all relative humidities, and any one water molecule in either phase may evaporate at any relative humidity at any time. However, the fraction of any time interval during which any particular sorption center is vacant is very small at high humidity and increases as the relative humidity decreases. While the sorption center is vacant, the network tends to collapse and saturate this site by a secondary bond between cellulose molecules. If this collapsing structural element is composed of relatively stiff chains and contains a number of water molecules, complete collapse cannot occur until all the sites within this element are vacant simultaneously. At high vapor pressures of the sorbate the probability of this occurrence is small, but it increases rapidly with decreasing vapor pressure and the chance of the network collapse increases. Thus sorption hysteresis is a manifestation of a "mechanical lag in the response of the network structure caused by the strong adsorption of molecules on geometrically important sites."[7] It follows that hysteresis effects at a given relative humidity are more probable for structural elements composed of inflexible molecules (e.g., cellulose and cellulose derivatives) containing a large number of strongly sorbed water molecules than for structural elements composed either of flexible molecules or of inflexible molecules with a relatively few strongly adsorbed water molecules. Thus, in conformity with results of Speakman and Saville[63] and Smith[15] on nylon and Taylor[64] on polyvinyl alcohol, hysteresis effects are negligible for networks of flexible molecules.

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[62] C. O. Seborg, *Ind. Eng. Chem.*, **29**, 169 (1937).

Taylor[64] has reported that hysteresis occurs over cycles between a dry fiber and one containing as little as 12.2 mg. water per gram of fiber. They point out that the mechanism for desorption discussed above requires sorption with some degree of grouping of the water molecules and question its applicability at low relative humidity. It is the author's opinion, however, that in view of the facts that the first molecules are probably adsorbed in the regions of poorest molecular packing and that even the first molecules cause swelling and therefore may act as a wedge for other molecules, some grouping of sorbed water molecules is likely even at low relative humidity.

Other phenomena of hysteresis, such as the effects of sample history and the attainment of equilibrium at intermediate points between the standard adsorption and desorption isotherms, are understandable on the basis of this theory. The irreversibility of the high primary desorption isotherm for undried cellulose fibers arises from the fact that water is distributed more or less homogeneously throughout the network during growth or precipitation from solution and that an irreversible crystallization by secondary bond formation between molecules occurs on the first drying.

(b) SORPTION AS A FUNCTION OF FIBER STRUCTURE

(1) Sorption of Water by Cellulose Fibers

For many years the sorption of water by cellulose was associated with "available surface," and changes in sorptive capacity accompanying various physical and chemical treatments were associated with changes in this "surface." As the concepts of the crystalline and amorphous nature of cellulose fibers developed, it became common practice to associate the water sorption capacity of a fiber with the crystallinity. In this view, the moisture regain of a fiber would decrease regularly with increasing crystallinity. More recently, it has been demonstrated that the "degree of crystallinity" of a fiber does not adequately describe the physical state of a cellulose fiber.[65,66] It is now accepted that such factors as crystal size and the nature of intermediate regions which are neither crystalline nor wholly amorphous in the usual sense do affect the moisture regain without affecting appreciably the crystallinity determined by other physical and chemical methods. For example, the crystallinity as measured by acid hydrolysis has a linear relation to moisture regain for both amine-treated cotton[67] and for a series of viscose rayons prepared by different methods.[68] For a given crystallinity, however, the viscose rayons always have a higher moisture regain than the cotton celluloses. This has been attributed to smaller crystals in regenerated cellulose and possible differences in the noncrystalline regions.[66] In this respect, Hermans[69] has proposed, and the author favors the viewpoint, that the disordered regions of various celluloses can exist in a number of different arrangements which allow greater or less sorption depending on the points of hydrogen bonding between molecules and the freedom to swell as sorption proceeds.

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[63] J. B. Speakman and A. K. Saville, *J. Textile Inst.*, **37**, P271 (1946).

[64] J. B. Taylor, *J. Textile Inst.*, **43**, T489 (1952).

There is a little doubt that the capacity of a given cellulose for moisture sorption is intimately connected with the submicroscopic structure of the cellulose. In general, the amount of moisture adsorbed at a given condition will depend upon the lateral-order distribution of the sample (as defined in Section B of this chapter) and the manner in which swelling accompanying sorption affects the local lateral order within the sample. The first factor apparently predominates and, as a first approximation, the total moisture adsorbed under given conditions will be a measure of lateral order and will increase with decreasing lateral order. For the most part, any change in moisture sorptive capacity of a given fiber as a result of physical or chemical treatments can be directly attributed to crystallization or decrystallization of the fiber during treatment. Swelling effects are also possible and will be discussed in a separate topic (see page 430).

The range of total sorption capacity normally encountered for various celluloses is illustrated by the data of Urquhart and Eckersall[70] in Figure 69

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[65] P. H. Hermans, *Contributions to the Physics of Cellulose Fibres*, Elsevier, New York, 1946, p. 51.

[66] J. A. Howsmon, *Textile Research J.*, **19**, 152 (1949).

[67] L. Segal, M. L. Nelson, and C. M. Conrad, *J. Phys. & Colloid Chem.*, **55**, 325 (1951).

[68] J. A. Howsmon, unpublished results.

[69] P. H. Hermans, *Physics and Chemistry of Cellulose Fibres*, Elsevier, New York, 1949, pp. 189–190.

and the approximate data in Table 18. As shown in Figure 69, both viscose rayon and mercerized cotton have a higher equilibrium moisture content than cotton at all relative humidity levels. As a first approximation,

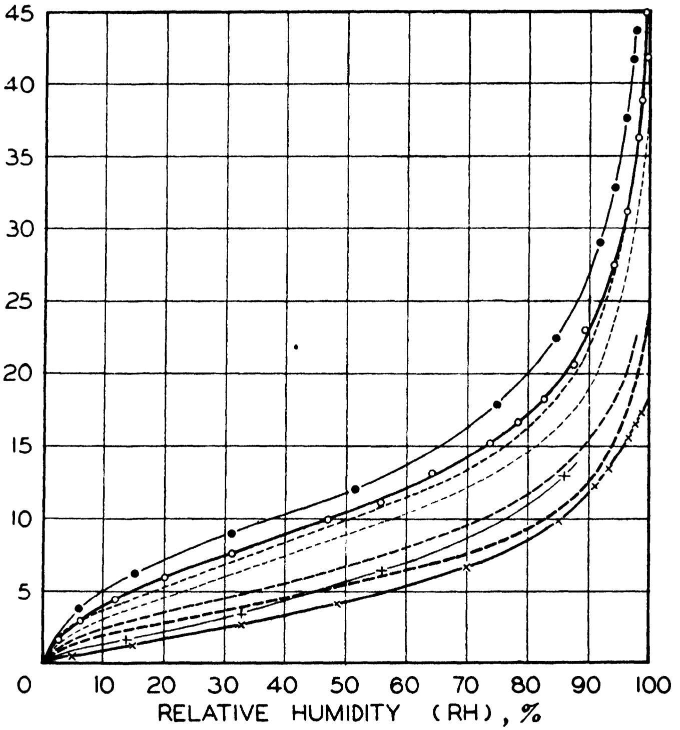

Fig. 69. Sorption isotherms of cellulose fibers (Urquhart and Eckersall[70]). Ordinate, per cent moisture regain.

Adsorption	Desorption	
——○——	——●——	Viscose rayon
——×——	——+——	Acetate rayon
▬ ▬ ▬ ▬ ▬ ▬ ▬	▬ ▬ ▬ ▬ ▬ ▬ ▬	Bleached cotton
- - - - - - - - - - -	- - - - - - - - - - -	Mercerized cotton

the sorption ratio which is the ratio of the moisture adsorption by any sample of cellulose to that of cotton at the same relative humidity, is directly proportional to the relative lateral order of the given sample and cotton at that humidity. This ratio is not constant over the entire humidity range but tends to be higher for viscose rayon at low relative humidity than at high relative humidity. The sorption ratio at any given humidity does, however, always give the same order of sorptive capacity for different celluloses. From the data in Table 18, the lateral order of the various materials can be said to decrease in the order: cotton linters, wood pulp, Fortisan, mercerized wood pulp, Fiber G, textile rayon, and high-tenacity rayon. The small variation of sorption ratio with relative humidity can be ascribed to differences in the manner in which swelling affects the lateral order for different samples.

TABLE 18

Moisture Regain and Sorption Ratio of Cellulose Fibers at 58% R.H. and 75°F. (Howsmon[66])

Sample	Moisture regain, %	Sorption ratio
Acetate-grade cotton linters.	6.70	1 00
Rayaceta wood pulp.	8.05	1 20
Fortisan.	9.60	1 43
Mercerized Rayaceta wood pulp.	10 45	1 56
Fiber G.	11.00	1.64
Textile rayon.	12.00–12.70	1 79–1 90
High-tenacity rayon.	12.70–13 70	1.90–2.05

As stated earlier, the actual values for moisture regain given in Table 18 can be considered only approximate because variations can occur within any of the general classes given depending upon the history of the sample. As a general rule, cotton fibers have the lowest moisture adsorption of all unmodified fibers. Cotton fibers from different sources do have different moisture regains for a given condition. These differences apparently arise from differences in growth conditions, drying conditions, or purification conditions but too few data are available to draw definite conclusions concerning each effect. In general, purification procedures reduce the hygroscopicity of cotton fibers. This effect may arise either from the removal of hygroscopic impurities or from crystallization which accompanies the purification procedure.

Wood pulps as a general class show definitely higher moisture adsorption than cotton at all values of relative humidity, but there is considerable variation in the moisture sorption capacity of different pulps. These variations for different pulps undoubtedly stem from variations in the pulping process. Unfortunately, process details are usually not given in the

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[70] A. R. Urquhart and N. Eckersall, *J. Textile Inst.*, **23**, T163 (1932).

literature and no definite conclusions concerning the relation between moisture adsorption and structure or purity of the wood pulps can be drawn.

The most thorough examination of water sorption by rayons is that of Urquhart and Eckersall[70] who studied eighteen different rayons. They found that the sorption ratios varied from 1.67 to 2.12 on adsorption and from 1.59 to 2.05 on desorption. At the time their study was conducted, however, the concepts of cellulose structure had not been developed to the point that these variations could be adequately correlated with sample history. More recent work indicates that variations in moisture regain such as those observed by Urquhart and Eckersall result directly from process variables during rayon manufacture. Hermans,[71] Rees,[58] and Guthrie[59] have shown that the moisture regain of viscose rayons decreases with increasing stretch applied during spinning. Similar work in the author's laboratory[68] has shown that the moisture regain of a viscose rayon (1) decreases with decreasing degree of substitution of the cellulose xanthate when spun, (2) increases with increasing zinc concentration in the spinning bath, and (3) decreases with increasing stretch. These results should be general for conventional viscose rayon spinning in a Muller bath but are not all inclusive. For example, the effect of stretch in decreasing hygroscopicity of rayons varies with both the degree of substitution and the zinc concentration. The stretch effect is less pronounced in low zinc baths or at low degree of substitution of the cellulose xanthate. Grinberg[72] studied model filaments of regenerated cellulose and could not find the above trends of moisture regain with either stretch or degree of substitution. These results again indicate the dependence of any one variable in the viscose process upon the other conditions, and the failure to observe a decrease of hygroscopicity with increasing stretch is attributable to the use of a nonregenerating $(NH_4)_2SO_4$ bath in his spinning trials. Present data indicate that regenerated cellulose structures with moisture regain at any value between 9.0% and 14.0% on the scale presented in Table 18 can be prepared by suitable choice of conditions, and that the regain value in each is a direct result of the lateral order produced by each manufacturing condition. Thus, the high regain of high-tenacity rayon indicates low lateral order, and a decrease in regain with increasing stretch indicates that molecular orientation during spinning causes a slight but definite irreversible crystallization.

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[71] P. H. Hermans, *Contributions to the Physics of Cellulose Fibres*, Elsevier, New York, 1946, p. 20.

[72] B. Grinberg, *Ann. chim. (Paris)*, 6, 489 (1951).

(a) Effect of Physical and Chemical Treatment on Water Sorption. Various physical and chemical treatments have been reported to influence the hygroscopicity of cellulose fibers. For all cases in which the chemical composition of the fiber is not changed by the treatment, a change in moisture regain can be attributed directly to changes in submicroscopic structure of the fiber. An increase in moisture regain usually reflects decrystallization; a decrease usually reflects either crystallization or removal of a highly adsorbing noncrystalline component of the structure.

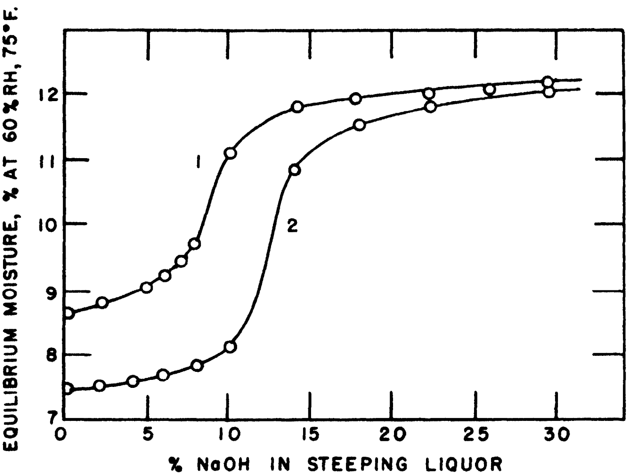

Fig. 70. Effect of per cent sodium hydroxide in steeping liquor on the equilibrium moisture content of cellulose recovered after steeping (Mitchell[75]). Curves: (1) sulfite wood cellulose (steeped at 20°C.); (2) cotton linters (steeped at 20°C.).

Marked reduction in hygroscopicity of all cellulose fibers follows degradation by hydrolysis with sulfuric[73] or hydrochloric acid.[74] This loss arises in part from the fact that the highly adsorbing noncrystalline regions are rapidly hydrolyzed to glucose and removed from the fiber and in part to the fact that the noncrystalline regions crystallize rapidly as hydrolysis proceeds.[66] High-temperature drying or treatment at high temperature in water vapor also reduces the hygroscopicity of fibers and, again, crystallization is indicated.

Mercerization of native cellulose fibers always causes an increase in sorptive capacity. Under certain conditions, the sorptive capacity of a native cotton can be increased by 50–60%, but the magnitude of the increase in any particular case is strongly dependent upon the temperature, concentration of the NaOH solution, and nature of the starting material. These effects are illustrated in Figure 70.[75] In any case, the increase in sorptive capacity with mercerization is compatible with decrystallization effects. When the highly swollen alkali cellulose is washed and dried, both the crystal size and the relative proportion of highly ordered regions are less than those present in the original fiber. On the other hand, treatment of a poorly ordered cellulose such as viscose rayon with alkali has been reported to result in a decrease in moisture sorption.[76]

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[73] S. E. Sheppard and P. T. Newsome, *J. Phys. Chem.*, **33**, 1817 (1929).

[74] R. F. Nickerson, *Ind. Eng. Chem.*, **33**, 1022 (1941); **34**, 85 (1942); **34**, 1480 (1942).

Mechanical beating of wet fibers, as usually carried out in the paper industry, produces no marked increase in moisture sorption[77] although prolonged beating does produce a slight increase.[78] Grinding of dry cellulose in a ball mill does produce pronounced increases in moisture sorption along with loss of fiber structure for either native or regenerated celluloses.[79] In every case the increase in moisture sorption is accompanied by a decrease in lateral order as indicated by x-ray diffraction.

(2) *Sorption of Nonaqueous Liquids*

Very few data on the sorption of nonaqueous liquids by cellulose fibers is available, and in many cases the data given by various investigators are inconsistent. These inconsistencies probably arise from the fact that sorption of nonaqueous liquids is strongly dependent on the moisture content of the sample and is, therefore, extremely sensitive to small variations in sample history and drying methods. The most comprehensive studies are those of Kanamaru and Chao[80] and Lauer[39] whose results are given in Table 19. The values given here are interpolated from data given by these authors and can be considered only approximate. The results are in general agreement with the work of other investigators. The sorption of alcohols by cellulose fibers decreases regularly with increasing molecular weight of the alcohol and becomes practically negligible with butanol.[81] The sorption of other liquids with no capacity for specific interaction with cellulose is usually small and does not change radically with increasing vapor pressure.[39,82,83] Lauer[39] has shown that (1) typical sigmoid sorption isotherms are obtained only on sorption of liquids such as methanol or ethanol which swell cellulose, and (2) liquids such as benzene, butanol, and chloroform give sorption isotherms that are entirely concave toward the vapor pressure axis. Both Lauer[39] and Richter, Herdle, and Wahtera[83] have shown that the constant differences between sorption of water by native, mercerized, and regenerated fibers are not found for most other liquids, and in many cases the order of sorptive capacity is reversed. For example, native fibers adsorb much more pyridine or acetic acid than either mercerized or regenerated fibers. This effect seems to be most closely related to fiber structure and the relative ease of swelling of different network structures.

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[75] R. L. Mitchell, *Ind. Eng. Chem.*, **43**, 1786 (1951).

[76] P. H. Hermans, D. Vermaas, and A. Weidinger, *Nature*, **165**, 238 (1950).

[77] L. M. Pidgeon and O. Maass, *J. Am. Chem. Soc.*, **52**, 1053 (1930).

[78] C. O. Seborg, F. A. Simmonds, and P. K. Baird, *Ind. Eng. Chem.*, **28**, 1245 (1936).

[79] P. H. Hermans and A. Weidinger, *J. Am. Chem. Soc.*, **68**, 2547 (1946).

[80] K. Kanamaru and J. Chao, *Kolloid-Z.*, **84**, 85 (1938).

[81] S. E. Sheppard and P. T. Newsome, *J. Phys. Chem.*, **36**, 2306 (1932).

TABLE 19

Sorption of Vapors by Cellulose Fibers[39,80]

	Maximum vapor sorbed (g./100 g.)			
	Cotton Relative vapor pressure		Viscose Rayon Relative vapor pressure	
Liquid	20%	90%	20%	90%
Water	2.2	10.1	7.0	28.8
Methanol	0.6	7.5	0.3	13.3
Ethanol	0.5	4.7	—	—
n-Propanol	0.2	0.85	0.15	1.2
n-Butanol	0.0	0.0	0.0	0.0
Ethyl ether	0.37	0.37	0.15	0.5
Acetone	0.04	3.0	0.7	1.3
Acetic acid	0.13	10.8	0.0	0.3
Benzene	1.0	1.2	0.0	0.5
Chloroform	0.91	1.1	0.0	0.5
Carbon tetrachloride	1.0	1.2	—	—

Many attempts have been made to correlate sorption and swelling of cellulose fibers with dielectric constant, surface tension, or dipole moment of the liquid but such correlation is possible only within families of compounds.[84] In studying the penetration of liquids into cellulose, Stamm and Tarkow[84] consider that the extent to which a given liquid will penetrate a fiber is dependent principally upon the molecular volume of the liquid and its ability to form hydrogen bonds with cellulose hydroxyl groups. It is the author's opinion that consideration of these factors and

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[82] N. H. Grace and O. Maass, *J. Phys. Chem.*, **36**, 3046 (1932).

[83] G. A. Richter, L. E. Herdle, and W. E. Wahtera, *Ind. Eng. Chem.*, **44**, 2883 (1952).

[84] A. J. Stamm and H. Tarkow, *J. Phys. & Colloid Chem.*, **54**, 745 (1950).

the nature of the network structure of different fibers (Section B of this chapter) makes possible an adequate explanation of most sorption phenomena for nonaqueous systems. Thus, small molecules which form hydrogen bonds will be strongly sorbed by cellulose fibers and this sorption will decrease with increasing molecular volume or other steric effects. Larger molecules which form hydrogen bonds can enter and swell more readily and to a greater extent a fiber in which the "amorphous" regions have exceedingly low lateral order than a fiber in which the "amorphous" regions have a relatively high lateral order. Since dry regenerated fibers as a rule have a very compact network structure with a large proportion of marginally "crystalline" material, the relatively low sorption of such vapors as pyridine and acetic acid by regenerated celluloses is explainable on this basis.[84] Larger molecules of either strong or limited hydrogen bonding ability can be readily sorbed in a fiber which has been preswollen with a liquid in which they are miscible. Small molecules with small hydrogen bonding tendencies will neither strongly adsorb on or swell cellulose fibers.

(3) *Sorption of Water by Cellulose Derivatives*

According to Sheppard and Newsome[85] the moisture regain of cellulose triesters decreases with increasing size of the substituent group and reaches a minimum with the triheptanoate. Further increase in size of the substituent group leads to a slight increase in regain. Sheppard and Newsome[73] also studied the relation between degree of substitution (D.S.) and moisture regain of cellulose acetates and found that the relation depended upon the method of preparation of the esters. They found a linear relation up to complete substitution for acetates prepared heterogeneously, whereas homogeneous acetylation yields acetates of higher moisture regain whose regain–D.S. curve was linear at intermediate D.S., but dropped off rapidly at high D.S. and met the curve for heterogeneous acetates at complete substitution. For both types of acetate the moisture regain decreased with increasing D.S. It has, however, been reported that both acetylated rag stock[86] and partially hydrolyzed acetate rayon[87] have a maximum moisture regain at about 4% combined acetic acid.

Similar results have been obtained for cellulose ethers. Lorand[88] found a linear relation between moisture regain and D.S. of ethyl celluloses for degrees of substitution greater than 0.5. The moisture regain decreased with increasing D.S. Lorand also found the moisture regain to diminish with increasing size of the substituent from the ethyl to the amyl ethers. Jayme and Froundjian[89] have reported that the moisture regain of methyl celluloses increases with increasing methoxyl content over the range from 0% to 10% methoxyl.

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[85] S. E. Sheppard and P. T. Newsome, *J. Phys. Chem.*, **39**, 143 (1935).

[86] W. H. Aiken, *Ind. Eng. Chem.*, **35**, 1206 (1943).

[87] J. Rosset and R. Paris, *Compt. rend.*, **228**, 920 (1949).

[88] E. J. Lorand, *Ind. Eng. Chem.*, **30**, 527 (1938).

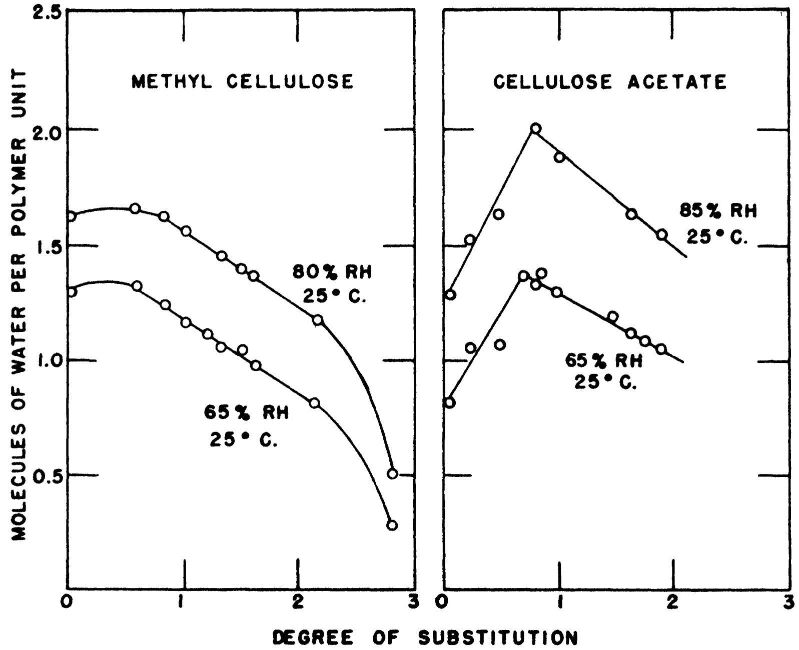

Fig. 71. Variation of moisture regain of methyl cellulose and cellulose acetate with degree of substitution (Gibbons[90]).

All of these observations indicate that the moisture regain of a cellulose derivative for a given condition is determined by the nature of the substituted group, the degree of substitution, the proportion of the unsubstituted hydroxyls which remain accessible in a partial ester, and the extent of crystallization in a triester. As in the case of cellulose itself, the moisture regain is independent of the molecular weight.[90]

These determining factors for moisture regain are illustrated by the data of Gibbons[90] in Figure 71. The observed effects should be general for all derivatives prepared by homogeneous reaction. The difference in moisture regain of the extremely low-D.S. samples, as expressed in molecules of water adsorbed per anhydroglucose unit, is merely a reflection of the tendency for regenerated celluloses prepared by saponification of cellulose acetate to be more crystalline and have lower regains than those prepared by the viscose process. As discussed previously for unmodified cellulose, the moisture regain increases with decreasing crystallization. The introduction of a larger side group on any cellulose hydroxyl will prevent a number of adjacent hydroxyl groups from forming hydrogen bonds and decrease the tendency of the material to crystallize. The increase in moisture sorption at low D.S. is, therefore, directly attributable to an increase in the number of hydroxyl groups which are available for water sorption. As the D.S. increases, the number of hydroxyl groups freed by each substituted group decreases so that the moisture regain reaches a maximum and then decreases. The disappearance of crystallization effects is marked by the beginning of the linear portion of the curve; over this range, the slope of the line is related to the relative affinity of water of the various substituents. Thus, the acetyl group has a lower affinity for water than the hydroxyl group, for otherwise the slope would approach zero. Similarly, acetyl groups are more hygroscopic than methoxyl groups as indicated by the steeper slope for methyl celluloses and the higher regain of cellulose acetate at a given D.S. Finally, at higher degrees of substitution, the molecules are approaching long-range uniformity and as crystallization takes place, inaccessible regions are again formed. This effect, combined with the substitution of the last hydroxyl groups, produces a rapid decrease in moisture regain. Although this departure from linearity at high D.S. is not shown in Figure 71, it has been reported for cellulose acetate by Sheppard and Newsome.[73]

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[89] G. L. Jayme and D. Froundjian, *Cellulosechemie*, **18**, 9 (1940).

[90] G. C. Gibbons, *Shirley Inst. Mem.*, **26**, 59 (1953); *J. Textile Inst.*, **44**, 201 (1953).

Heterogeneous reactions produce different effects than those illustrated. Sheppard and Newsome[73] found that cellulose acetates prepared heterogeneously had lower regain at a given D.S. than those prepared homogeneously. Heterogeneously acetylated cellulose[73] and ethyl celluloses[88] also showed linear decreases in moisture regain up to complete substitution. In heterogeneous reactions, substitution occurs more rapidly in regions immediately accessible to the reactants and in the early stages the decrease in regain must arise from the decrease in the number of the hydroxyl groups in these accessible regions. At this stage, the originally inaccessible regions are only slightly affected. The reaction must continue by a process of opening up inaccessible regions with almost simultaneous reaction of the freed hydroxyl groups.

(4) *Sorption of Nonaqueous Liquids by Cellulose Derivatives*

As in the case of moisture sorption, the nature and amount of a nonaqueous vapor adsorbed by a cellulose derivative will depend upon the nature of the substituent group, the degree of substitution, and the extent of crystallization in the derivative. Actually, true sorption data are rather limited for most work has been confined to qualitative study of the solubility of various derivatives in various solvents.

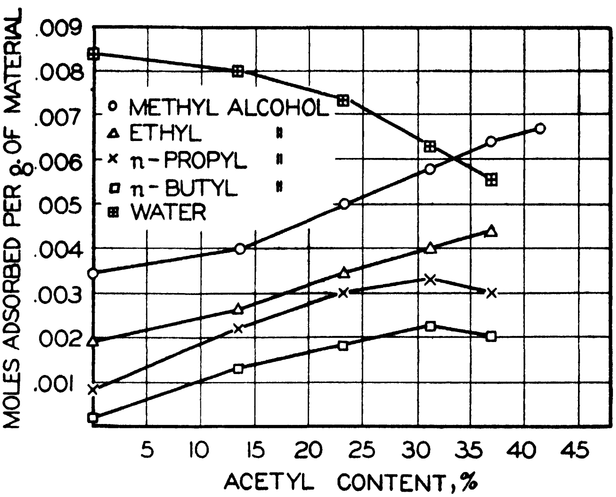

Fig. 72. Adsorption of alcohols by cellulose acetate as a function of acetyl content (Sheppard and Newsome[81]).

Sheppard and Newsome[81] studied at saturation pressures the sorption of water and alcohols by cellulose acetates of varying acetyl content. Their results, given in Figure 72, show that for various alcohols the moles adsorbed per gram of material increase with increasing acetyl content and decrease with increasing length of the alkyl group. These results indicate that at low degree of substitution (D.S.) the interaction of sorbate with the cellulose hydroxyls contributes most to sorption. As the D.S. is increased the interaction of alkyl groups begins to yield an increasing contribution to the sorption; at complete substitution, the interaction of the sorbate with the acetyl groups is the determining factor.

Actually, there appears to be close correlation between sorption of various liquids by a given derivative and the solubility of the derivative in the liquid. McBain and coworkers[20] studied the sorption of twenty-three different vapors by nitrocellulose and found sorption at 90% relative vapor pressures ranging from 1% to about 100% by weight. From their work, it is clear that good solvents for nitrocellulose such as butyl acetate or acetone are extensively sorbed and that indifferent liquids such as water or hexane are poorly sorbed. Poor solvents which swell the material occupy an intermediate position. The sorption isotherms over the entire vapor pressure range for good solvents have a pronounced sigmoid shape. The sigmoid shape becomes less pronounced for intermediate solvents, and the isotherm for indifferent liquids is entirely concave to the vapor pressure axis as expected for strict surface adsorption. These observations offer some support to the general solution mechanism for sorption phenomena. Kanamaru and Chao[80] made similar studies for cellulose triacetates, secondary cellulose acetates, and nitrocelluloses but did not find close correlation with solubility of their materials although qualitative correspondence is good. Variations in this correlation may arise from crystallinity effects which will be more pronounced in sorption than in solution or from the fact that rate of attainment of equilibrium is sometimes very slow in films as compared to precipitated flaky materials.[81]

(c) SORPTION AND SWELLING

(1) *Volume Contraction during Swelling*

It is well known that swelling of fibers begins at the onset of water adsorption and that in the initial stages of sorption the total volume of the system is less than the volume of the dry fibers plus the volume of the adsorbed liquid. This effect is encountered in measurements of the density of fibers by liquid displacement in that the density varies with the immersion liquid used. Davidson[91] found densities for cotton fibers of 1.567, 1.550, and 1.6095 and for viscose rayon of 1.548, 1.543, 1.6084 in helium, toluene, and water, respectively. A prevalent interpretation of these results has been to consider the density in helium as the true density because the helium should be able to penetrate into the smallest pores in the structure and should not be bound to the structure by any forces except van der Waals forces. Toluene cannot penetrate completely into the structure and, hence, the density is too low. Water, however, can penetrate completely, but is adsorbed strongly on cellulose hydroxyl groups and the fraction so absorbed is considerably compressed. The density in water is, therefore, too high. From the difference in density in helium and in water the apparent density of the compressed water can be calculated. From Davidson's data, the density of the sorbed water appears to be about 5 to 7% higher than that of free water.

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[91] G. F. Davidson, *J. Textile Inst.*, **18**, T175, T275 (1927).

As a proof of the reality of the contraction, Filby and Maass[92] determined the density of cellulose fibers at different water contents. They found that the contraction was greatest for the first water adsorbed and disappears at about 9% water beyond which additional water sorbed added its normal volume to the system. They calculated that the sorbed water at 3% moisture had an apparent density of 2.60. The density dropped off rapidly with increasing moisture content and is 1.0 above 9% water. It has been estimated that pressures of the order of 11,000 to 14,000 atmospheres would be required to compress liquid water to the same extent.[92,93]

Hermans[94] reviewed these concepts and studied the density of regenerated cellulose at various water contents. The apparent density of the sorbed water was found to be about 1.60 up to about 4% water. It diminished rapidly with increasing water content but does not reach the normal value of 1.0 until 20 to 25% water has been added. Hermans rejects the compression of water as having little physical significance and offers a different interpretation.

He points out that density loses its significance when applied to substances containing holes of molecular dimensions for which the molecular volume of the immersion fluid will be a significant factor. He considers the density in inert liquids such as toluene or benzene which do not swell cellulose as the true density in the usual sense. The high density in water arises from the ability of the amorphous regions of the fiber to form a homogeneous molecular dispersion in water. The apparent volume contraction then arises from a more efficient packing of cellulose and water molecules which this dispersion brings about. According to this interpretation, the compression of sorbed water is illusory.

It is the author's opinion that this interpretation is more plausible than the compression theory. It seems more consistent with solution theory for mixing of molecules and does not require the extremely high densities and pressures which must be postulated if the volume contraction were considered to be attributable only to water. The actual volume contraction must be related to both cellulose and water. The fact that the number of hydrogen bonds per unit volume of sorbed water is greater than the number present in the same volume of liquid water also leads to a volume contraction in the water-cellulose system analogous to that observed with alcohol and water.

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[92] E. Filby and O. Maass, *Can. J. Research*, **7**, 162 (1932).

[93] A. J. Stamm and R. M. Seborg, *J. Phys. Chem.*, **39**, 133 (1935).

[94] P. H. Hermans, *Contributions to the Physics of Cellulose Fibres*, Elsevier, New York, 1946, pp. 73–86.

(2) *Changes in Fiber Dimensions*

Although the work by density methods shows that as a first approximation the swelling of a fiber on sorption of water is equal to the volume of water added, actual changes in fiber dimensions are of great practical interest. This interest stems largely from the fact that the increase in length of a fiber on swelling is much smaller than the increase in width. Both the total volume swelling and the swelling anisotropy are technically important because of their relation to fabric shrinkage. Volume swelling of fibers may be studied microscopically in two ways: (1) by observing the increase in diameter from the side of the fiber, or (2) by measuring the increase in area of a thin cross section. Because of the irregular shape of the cross section, the latter method is more exact. Changes in length are usually followed microscopically. As a general rule, systematic errors in measuring swelling are large and no great precision can be claimed for the results.

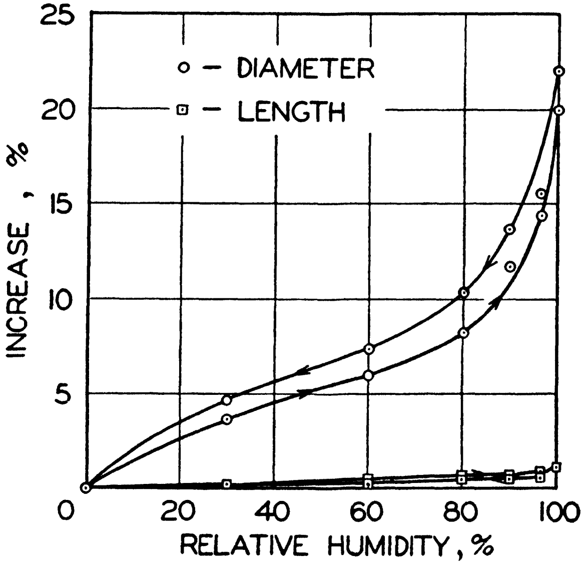

Fig. 73. Dimensional changes of cotton during sorption of water (Collins[42]).

Collins[42] investigated both length and diameter swelling of cotton fibers over the entire humidity range. The mean values of his observations are given in Figure 73. It is apparent from these results that the diametric swelling follows the shape of the sorption isotherm closely and that hysteresis is also shown by the dimensional changes. Similar results for viscose rayon are shown by the data of Morehead[95] in Table 20. The linear swelling of various viscose rayons may vary from 0.7 to 8.0%, but most commercial rayons will fall in the range from 0.7 to 4% linear swelling.

TABLE 20

Cross-Sectional Swelling of Viscose Rayon as a Function of Relative Humidity (Morehead[95])

Relative humidity	High-tenacity rayon		Experimental rayon[a]	
	Adsorption	Desorption	Adsorption	Desorption
0 7	0.0	0.0	0.0	0.0
20	1 4	2.2	0.4	4 5
60	2 2	8.0	4.9	13.4
80	16 9	15.5	11.7	19.6
90	21.1	23.6	12 5	23.0
97	25 9	42.6	17.6	27.2
Wet	91.5	91.5	43.9	43.9

[a] Highly crystalline, highly oriented viscose rayon.

The anisotropy of swelling can be regarded as a measure of the orientation of the structural elements of a fiber in respect to the fiber axis. Hermans[96] and Hermans and DeLeeuw[97] investigated the relation between orientation and swelling anisotropy. They prepared isotropic cellulose fibers by extruding viscose under low pressure with no stretch into a coagulating bath. Both length and diametric swelling were about 26%. Oriented fibers were prepared by stretching these isotropic filaments. With increasing stretch the swelling became more anisotropic. The swelling in length was reduced to about 1%, and the swelling in width increased to 40%.

Comparative values for the cross-sectional swelling from the data of Morehead[98] are given in Table 21. The difference in magnitude of the values in Tables 20 and 21 arises from the common practice of expressing cross-sectional swelling in terms of partially swollen fiber conditioned at moderate relative humidity rather than in terms of the dry fiber as done in

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[95] F. F. Morehead, *Textile Research J.*, **22**, 535 (1952).

[96] P. H. Hermans, *Kolloid-Z.*, **86**, 107 (1939).

[97] P. H. Hermans and A. J. de Leeuw, *Kolloid-Z.*, **81**, 300 (1937).

[98] F. F. Morehead, *Textile research J.*, **17**, 96 (1947).

Table 20. Since the axial swelling of most of these fibers is small, these values represent approximate total relative volume swelling of these fibers. In view of the definite relations previously discussed between sorption and crystallinity and sorption and swelling, it would be expected that the total volume swelling should be a measure of the total disorder or amorphous nature of the fiber. This is approximately true for swelling and sorption at low relative humidity, but wide deviations occur at high relative humidity and in the wet condition.

TABLE 21

Cross-Sectional Swelling of Cellulose Fibers in Water (Morehead[98])

Fiber	Cross-sectional swelling, %
Cotton linters	21
Mercerized cotton	24
High-tenacity viscose rayon	50
Textile viscose rayon	65
Cuprammonium rayon	56
Lilienfeld rayon	45
Fortisan	22
Cellulose acetate rayon	8
Viscose rayon (resin treated)	30–40

In this connection it should be noted that on immersion in water there is a very large increase in swelling of a fiber previously conditioned at 100% relative humidity. This effect is shown by the data in Table 20, and the phenomena are general for all cellulose fibers. In general, as expected from the relative crystallinity of cotton and rayon, rayons have much larger swelling in water than cotton. That a direct relation between final water swelling and crystallinity alone does not exist is indicated by the intermediate position (Table 21) of high-tenacity rayon which is generally considered the least crystalline cellulose fiber. The ultimate swelling of a rayon fiber can also be reduced by cross-linking or resin impregnation treatments. Cameron and Morton[99] have reported that one cross-link for every 100 anhydroglucose units in viscose rayon will reduce the total swelling capacity from 90–100% to 45–50%. Similarly, Richter, Herdle, and Wahtera[83] have reported that formaldehyde treatments of wood and cotton celluloses reduced the water sorption at 95% relative humidity to two thirds and acetic acid sorption to one third of the value for untreated controls. In many cases of this type, the moisture regain and swelling at low and intermediate relative humidity is only insignificantly lowered by these treatments, and again decreased sorption and swelling at high relative humidity or in water cannot be attributed to "amorphous" cellulose in the usual sense. It has frequently been mentioned in the literature that heat-treatment or steam treatments greatly reduced the total swelling of viscose rayon. Hubert, Matthes, and Weisbrod[100] found that treatment of regenerated fibers with saturated steam at 100°C. reduced the swelling to about 50–55%. Once more this reduction in swelling power is accomplished with little or no change in the sorption of water by the fibers at low and intermediate relative humidity.

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[99] W. G. Cameron and T. H. Morton, *J. Soc. Dyers Colourists*, **64**, 329 (1948).

It is apparent that the ultimate swelling of cellulose at high relative humidity or in water cannot be directly related to the proportion of noncrystalline cellulose present. This final swelling value is more probably dependent upon the geometry of the network structure of the fiber. Hermans[101] has proposed that amorphous regions in cellulose fibers can assume different arrangements which vary with the conditions of growth or precipitation, and are capable of greater or lesser swelling and sorption depending upon the number of chain contacts and freedom to swell as sorption proceeds. The author concurs with this viewpoint and feels that most of the observed swelling effects can be qualitatively explained on the basis of variations in lateral-order distribution discussed in Section B of this chapter. A network structure comprised of small ordered regions and small disordered regions would be expected to swell less in water than one comprised of large ordered regions separated by large disordered regions. The low swelling of high-tenacity rayon is probably directly attributable to effects of this type. Similarly, there are probably many places in a fiber structure where a high degree of short-range crystallization exists. Such regions may be too small to be considered crystalline in the usual sense, but correspond closely to description as highly ordered "amorphous" regions in contrast to pure random arrangements usually considered amorphous. The presence of such regions will affect swelling in much the same manner as a chemical cross-link. The pronounced reduction in swelling which accompanies formaldehyde treatments or steam treatments can, therefore, be pictured as a restriction in swelling capacity caused by the formation during treatment of true cross-links or of permanent crystallization effects which act as cross-links.

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[100] E. Hubert, A. Matthes, and K. Weisbrod, *Kolloid-Z.*, **98**, 173 (1942).

[101] P. H. Hermans, *Physics and Chemistry of Cellulose Fibres*, Elsevier, New York, 1949, pp. 189–194.

3. Effect of Moisture on the Physical Properties of Cellulose Fibers

(a) MECHANICAL PROPERTIES

The mechanical properties of fibers are of primary technological importance for they determine the reaction of the fiber to the various mechanical stresses encountered in use. The mechanical properties of cellulose fibers are strongly dependent upon the moisture content but no general relationship between moisture content and a given property can be applied to all cellulose fibers. Apparently, the chemical composition and submicroscopic structure of the fiber determine not only the amount of water adsorbed by the fiber, but also the manner in which this water affects the physical properties. As a general rule, both the tenacity and elongation at break of native cellulose fibers increase with increasing moisture content, whereas for regenerated fibers, the tenacity decreases and elongation increases with increasing moisture content. It has been suggested that moisture not only plasticizes the fiber by decreasing the number of secondary bonds between cellulose molecules but also allows more uniform distribution of strain over the cross section of the fiber. The relative importance of these two effects determines whether the tenacity will increase or decrease with increasing moisture content.

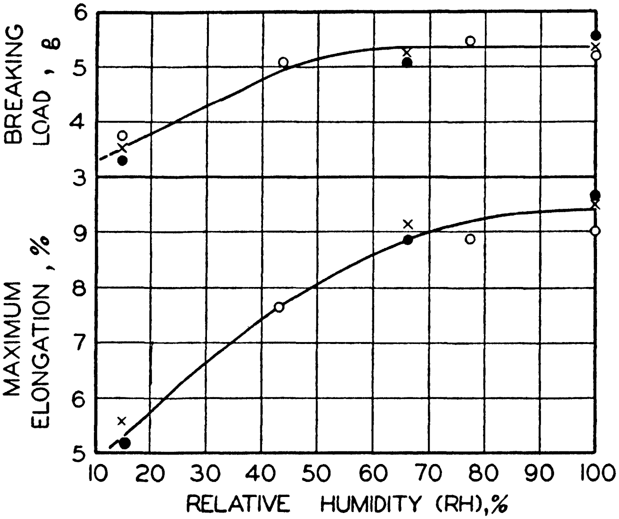

Fig. 74. Tensile strength and elongation of single cotton fibers as a function of relative humidity (Brown, Mann and Pierce[102]).

The influence of varying moisture content on the breaking strength and elongation of single cotton fibers is shown by the data of Brown, Mann, and Pierce[102] in Figure 74. The breaking strength of wet cotton fibers is even greater than expected from the data in Figure 74 and is usually of the order of 1.1 to 1.2 times the breaking strength at 65% relative humidity. The elastic modulus decreases with increasing moisture content. The tendency for both strength and elongation to increase and elastic modulus to decrease with increasing moisture content is general for native cellulose fibers. The molecules in these fibers are packed in uniformly high lateral order and, apparently, in the dry state the high rigidity of this structure causes premature breaks at low stress. As moisture is added, the structure is plasticized so that various structural elements move more easily under applied stress. The applied stress is, therefore, distributed more evenly over the fiber cross section, and higher strengths and elongations result.

The effect of relative humidity on the stress–strain behavior of rayons has been extensively investigated.[103–106] In the range from 40 to 75% relative humidity, Bellinson[103] found linear increase in tenacity and linear decrease in elongation with decreasing relative humidity. Bohler[104] states that the tenacity increases from 12.5 to 6% moisture and then decreases from 5 to 4% moisture whereas the elongation decreases over the same range with a critical point at 9% moisture. The elastic modulus decreases rapidly with increasing moisture content.

A comprehensive study of the effects of moisture content on the physical properties of a large number of modern viscose rayons has been carried out in the author's laboratory. This work shows that the effect of moisture on physical properties is strongly dependent upon the submicroscopic structure which, in turn, is dependent upon the manufacturing conditions. In all cases, the tenacity increased linearly with decreasing water content over the range from 15 to 6% water and reached a maximum at some point below 6% water. The water content at maximum tenacity varies regularly with spinning conditions and is usually lower for rayons of high lateral order than for rayons of low lateral order. The elongation at break for rayons spun with low stretch decreases linearly with decreasing water content over the range from 15 to 6% water, but as the water content decreases further the elongation decreases rapidly in the same manner as that shown for cotton in Figure 74. The elongation of rayons spun with high stretch decreases linearly over the whole range from 15 to 0.5% water.

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[102] K. C. Brown, J. C. Mann, and F. T. Pierce, *J. Textile Inst.*, **21**, T187 (1930).

[103] H. R. Bellinson, *Textile Research*, **10**, 372 (1940).

[104] K. Bohler, *Kunstseide*, **13**, 397 (1931).

[105] H. Hindman and K. R. Fox, *Rayon Textile Monthly*, **24**, 235, 287 (1943).

[106] E. Thielmann, *Melliand Textilber.*, **21**, 61 (1940).

The plasticization of rayon fibers by adsorbed water may show its effect on physical properties in any one of a number of ways lying between two extreme conditions: (1) a regular decrease in tenacity and only small changes in elongation with increasing water content, and (2) a regular small decrease in tenacity with large increases in elongation with increasing water content. Both these conditions and intermediate cases can be qualitatively related to the lateral-order distribution within the fiber. For example, rayon yarns comprised of large perfect crystals separated by large poorly ordered regions (heterogeneous lateral-order distribution) usually show pronounced decreases in tenacity and small increases in elongation with increasing water content. Apparently, the applied stress is most evenly distributed in the dry fiber. Added water plasticizes the poorly ordered regions preferentially so that with increasing water content the stress distribution over the fiber cross section is less uniform and a sharp decrease in tenacity results. Such systems usually have low ratios of wet-to-dry tenacity. Rayon fibers comprised of small ordered regions and small relatively highly ordered amorphous regions (homogeneous lateral-order distribution) usually show large changes in elongation and smaller decreases in tenacity with increasing water content. Such systems usually have higher ratios of wet-to-dry tenacity than systems of heterogeneous lateral-order distribution. High lateral-order fibers with homogeneous lateral-order distribution and high orientation such as Fortisan also show high ratios of wet-to-dry tenacity but usually show no marked increase in elongation with increase in moisture content.

Thus, the effect of moisture on the physical properties of a cellulose fiber is a complex function of the distribution of strain over the fiber cross section, the plasticizing effects of adsorbed moisture, and the submicroscopic structure of the fiber. As a general rule, addition of water to relatively brittle natural fibers of high lateral order allows more uniform distribution of strain and both tenacity and elongation increase with increasing water content. The relatively low lateral-order fibers such as viscose rayon are easily plasticized by sorbed water and in the general case the tenacity decreases and elongation increases as water is added. Uniform lateral-order distribution in these fibers at either high or low levels of order favors high wet strength and relatively high wet elongation whereas nonuniform lateral-order distribution usually results in low wet strength and low wet elongation. A more complete discussion of these effects is given in Chapter XI.

(b) ELECTRICAL PROPERTIES

The electrical resistance of both cellulose fibers and cellulose derivatives is extremely sensitive to changes in moisture content. This is illustrated in Figure 75 by the data of Murphy and Walker[107] for cotton fibers. The resistance decreases from about 10^{16} ohms at 5% relative humidity to about 10^7 ohms at 95% relative humidity. As expected from the difference in equilibrium moisture content on adsorption and desorption, hysteresis is pronounced. If the resistance is plotted against moisture content, however, the adsorption and desorption curves shown tend to be superimposed Hearle[108] has recently reexamined most of the published data on electrical

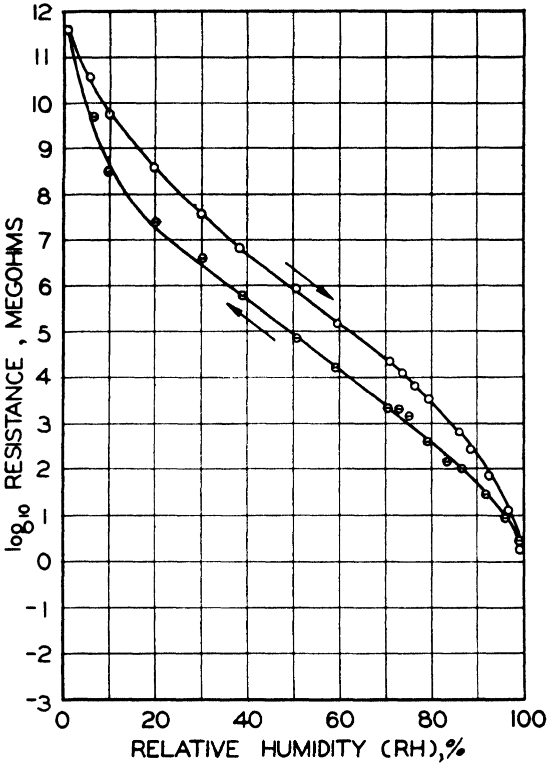

Fig 75. Insulation resistance of cotton threads as a function of relative humidity (Murphy and Walker[107]).

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[107] E. J. Murphy and A. C. Walker, *J. Phys. Chem.*, **32**, 1761 (1928).

[108] J. W. S. Hearle, *J. Textile Inst.*, **43**, P194 (1952).

resistance of cellulose fibers. Exact comparisons of resistance of different fibers is difficult because different workers frequently express their results in terms of the resistance of samples of different dimensions. Hearle[108] found, however, that the relation between resistance and moisture content for cellulose and most other fibers could be generally expressed in the form:

$$\log R_s = -n \log M - \log K$$

where R_s is the mass specific resistance, M is the moisture content of the fiber (weight of water divided by the weight and fiber plus water), and n and K are constants. This linear relationship holds over the range from 3 to 25% water. Many theories of conduction in cellulose fibers have been proposed but there is no generally accepted theory. It is obvious, however, that cellulose and cellulose derivatives themselves are good insulators and that the conduction of electric current is principally dependent upon the adsorbed moisture and the distribution of this moisture through the fiber structure. The pronounced changes in conductivity of cellulose with

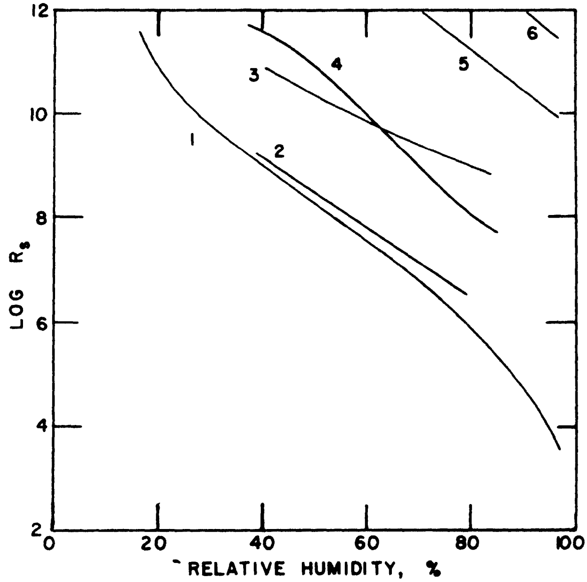

Fig. 76. Approximate relationship between log R_s (mass specific resistance) and relative humidity for various fibers (Hearle[108]). Curves: (1) cotton; (2) viscose rayon; (3) nylon; (4) wool; (5) acetate rayon; (6) Cotopa 60 (cellulose triacetate).

changing moisture content and the exact nature of the relationship between moisture content and conductivity is utilized in the determination of the moisture content of celluloses by electrical meters.[109,110]

An approximate comparison of the resistance of different fibers under identical external conditions is given in Figure 76 by a plot of log R_s versus relative humidity. Acetylation of cotton reduces the moisture regain at a given relative humidity and, therefore, greatly increases its resistance at that humidity. Cellulose triacetate has very high electrical resistance at relative humidities approaching saturation. This effect is apparently general for cellulose esters. Similarly, any physical or chemical treatment which lowers the moisture regain of cellulose without changing its chemical composition will increase the electrical resistance at a given relative humidity. The increase in resistance will usually be less than that which accompanies esterification.

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[109] R. K. Toner, C F Bowen, and J. C. Whitwell, *Textile Research J.*, **18**, 526 (1948).

[110] E. H Jones, *J Sci Instruments*, **17**, 55 (1940).

Chapter V

PROPERTIES OF SUBSTANCES ASSOCIATED WITH CELLULOSE IN NATURE

A. THE PHYSICAL AND CHEMICAL NATURE OF WOOD

HARRY F. LEWIS AND GEORGE J. RITTER

Wood is an excellent source of structural material; it is light and easily sawed, cut, planed, shaped, steamed, bent, plasticized, molded, fabricated, and assembled by means of nails, screws, and glue. Wood is also an efficient insulator for sound and electricity, which is of prime importance in structural materials. These desirable properties of wood are due in large measure to its structure.

Wood is likewise the most important single source of cellulose fiber in the manufacture of pulp and paper by reason of its availability as a low-cost raw material, the advanced stage of the technology employed in converting wood into a fibrous condition, and the ease of converting the fiber into a continuous dry sheet at a relatively low cost. It is also the largest source of cellulose for chemical conversion for somewhat the same reasons.

1. Capillarity of Wood

Wood is extremely porous. An idea of its porous nature is obtainable without a microscopical examination. For example, the average specific gravity of dry blocks of wood from a large majority of species is approximately 0.5, whereas that of the dry substance is approximately 1.5. Thus, the ratio of the two specific gravities indicates that about two-thirds of any wood specimen is composed of air cavities. Immersion of the dry specimen in boiling water displaces the air and causes the wood specimen to sink.

The cavities in which air accumulates when water is removed from wood during drying are the lumens of the various cells and also the intercellular spaces at the junction of three or more cells. These cavities form the gross capillary system of wood and are the reservoirs for free water in water-soaked wood.

Water is also taken up in a much more intimate manner by wood. To some extent this is due to the swelling of the amorphous portion of the cellulose, and possibly of the hemicelluloses. Because of this swelling, there also seems to be a loosening of bonds between the structural elements of the wood, so that fine passageways are opened up. It may be estimated that the increase in volume of the dry wood substance when saturated with water is about 45%. The swelling and shrinkage of wood during the sorption and desorption of water are associated with these effects.

2. Wood Structure

The structural elements of the hardwood or broad-leaved species (angiosperms) differ considerably from those of softwoods or needle-leaved species (gymnosperms) both in morphology and size. These differences are apparent from a study of Figures 1, 2, and 3 and Figures 4, 5, and 6 which represent transverse, radial, and tangential sections of yellow poplar and white spruce, respectively.

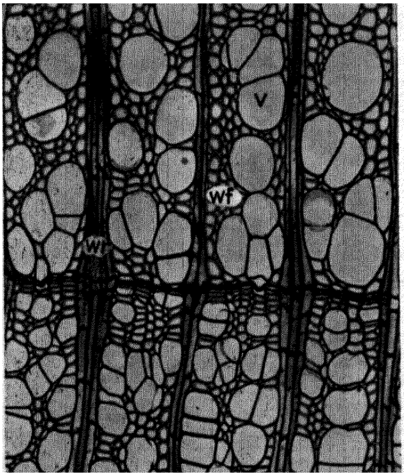


Fig. 1. Photomicrograph showing cross section of yellow poplar. Magnification ×75. v = vessel; wf = wood fiber; wr = wood ray.

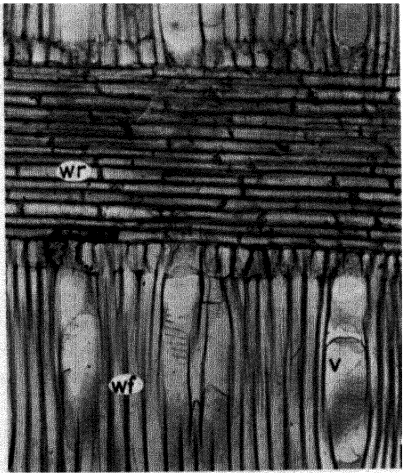


Fig. 2. Photomicrograph showing radial section of yellow poplar. Magnification ×75. v = vessel; wf = wood fiber; wr = wood ray.

The transverse sections show that wood is, generally speaking, a heterogeneous cellular structure consisting of zones, known as annual rings, each of which represents the radial growth of the tree during one year. The

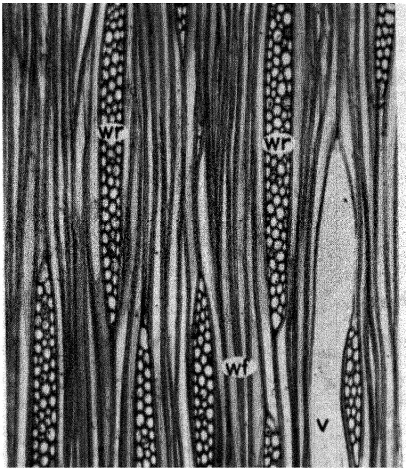


Fig. 3. Photomicrograph showing tangential section of yellow poplar. Magnification ×75. v = vessel; wf = wood fiber; wr = wood ray.

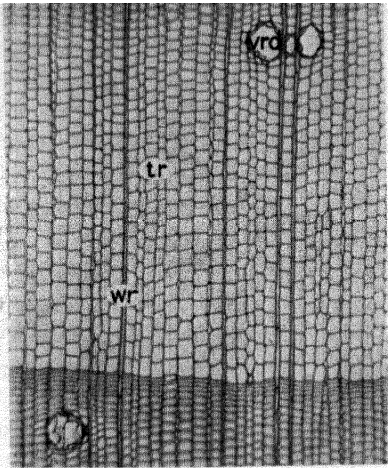


Fig. 4. Photomicrograph showing cross section of white spruce (*Picea glauca*). Magnification ×50. tr = tracheid; wr = wood ray; vrd = vertical resin duct.

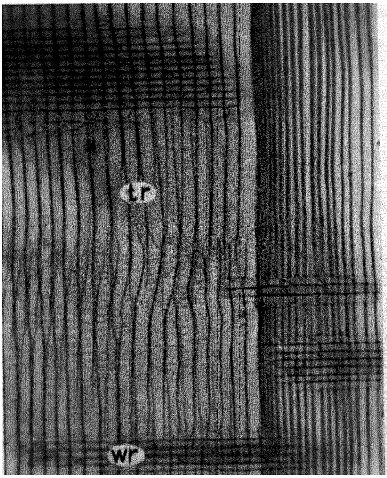


Fig. 5. Photomicrograph showing radial section of white spruce (*Picea glauca*). Magnification ×50. tr = tracheid; wr = wood ray.

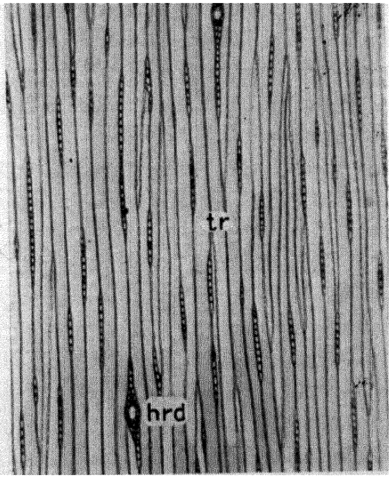


Fig. 6. Photomicrograph showing tangential section of white spruce (*Picea glauca*). Magnification ×50. tr = tracheid; hrd = horizontal resin duct.

main cause of the heterogeneous structure is the variation in the relative size of the cell cavities of the wood. If the ratio of the cell cavities to the cell wall is small, the wood appears dense; if the ratio of the cell cavities to the cell wall is large, the wood appears to be porous and is light in weight.

Both hardwoods and softwoods are composed of cells arranged in two systems. One system is longitudinal, that is, parallel to the long central axis of the tree. The other system is radial, that is, perpendicular to the long central axis of the tree. The two systems in the hardwood differ in some respects from those in the softwood.

Cells of the longitudinal system in the hardwood consist of wood fibers (*wf*) and vessels (*v*), which are seen in Figures 1, 2, and 3. The fibers that have large cavities develop during the early part of the growing season and form the springwood portion of the annual ring. The fibers that have small cavities develop during the late part of the growing season and form the summerwood portion of the annual ring. Vessels consist of cylindrical or ringlike segments arranged to form tubes which have diameters considerably greater than those of the fibers. These tubes are connected end-to-end to form long cylinders which function as longitudinal conductors of liquids in the tree. Vessels in some of the woods, such as white oak, are filled with inflated balloon-like projections called tyloses. These balloon-like structures are formed by a protrusion of the middle lamella, an intercellular cementing material, through the pit orifice into the vessel cavity. In commercial practice these tyloses retard the impregnation of the wood with preservatives.

The radial cellular system of hardwoods consists of wood rays (*wr*) which are composed of short slender ray cells arranged with their long axes radially in the tree. They are the conductors of liquids between the bark and the center of the tree in both directions and further act as a storehouse for plant food.

Softwoods have a longitudinal cellular system consisting principally of tracheids (*tr*) and resin ducts (*vrd*) (Figs. 4, 5, and 6). The tracheids that develop during the early growing season have large cell cavities and form the springwood, whereas those that develop in late growing season have small cell cavities and form the summerwood. Tracheids of the softwoods are arranged in better radial alignment than are the fibers in the hardwoods. Their cross sections have an approximately rectangular shape, whereas those of the hardwood fibers more nearly approach a pentagonal or circular shape. Vertical resin ducts also form a part of the longitudinal cell system of softwoods; they are much larger in diameter than the tracheids. As the name indicates, they form storage space for wood resins.

The horizontal cell system of the softwoods consists of wood rays (*wr*) (Figs. 4, 5, and 6), which are composed of short blunt ray cells and, in some cases, also of horizontal resin ducts (*hrd*). Wood rays having horizontal resin ducts are broad in the tangential direction of their cross sections and are known as fusiform wood rays because of the shape of their cross sections.

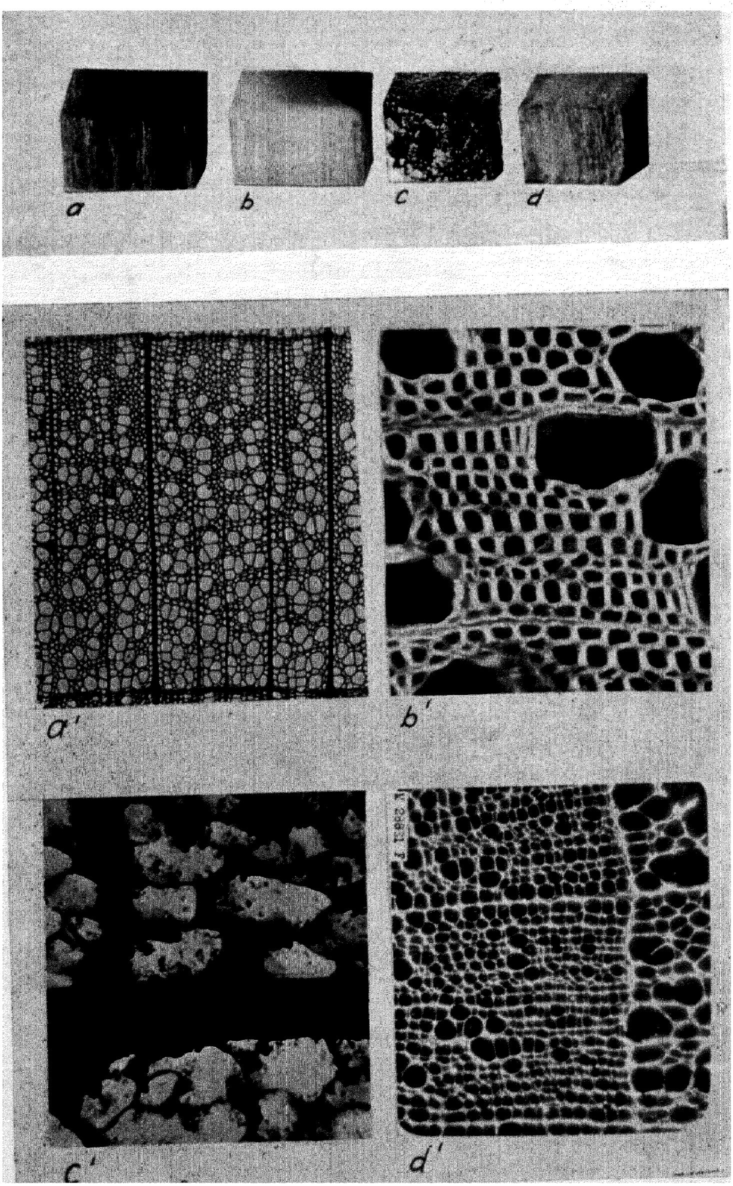
The cells of the two systems, in both hardwoods and softwoods, are held together by the middle lamella. Communication between the various fibers, vessels, tracheids, and ray cells takes place through pits in the cell walls, through pores in the middle lamella, and also through the ray cells. In softwoods, these ray cells are perforated by simple and bordered pits; in hardwoods, the pits are mostly of the simple type and are smaller than those in softwoods.

3. Important Chemical Constituents of Wood

The chief chemical constituent of wood is cellulose. Lignin and the hemicelluloses together about equal the cellulose in amount. These three fractions make up the wood structure, which is infiltrated with water-soluble, alcohol-soluble, and ether-soluble substances termed extractives. Small amounts of ash-forming minerals are also present and are distributed throughout the wood structure. These minerals, together with the lignin and the holocellulose, are so uniformly interspersed that any one of them alone forms a microstructural pattern of the wood. Thus, Figure 7 shows small blocks approximately 3 mm. on each edge which have been freed of their infiltrated substances. Specimen *a* is a photograph of a block of wood freed of its infiltrated materials. Specimen *b* is the holocellulose (hemicellulose plus cellulose) residue from a duplicate of specimen *a;* it was prepared by removing the lignin by means of alternate treatment with chlorine and alcohol–monoethanolamine solution. Specimen *c* is the lignin residue from a duplicate of specimen *a;* it was prepared by removing the holocellulose by means of sulfuric acid. Specimen *d* is the ash residue obtained by burning all the organic material in a duplicate of specimen *a;* it is equivalent to 0.5% by weight of the dry wood. It is extremely porous and light on account of the high proportion of air cavities in relation to the solids. Specimens *a′*, *b′*, *c′*, and *d′* are, respectively, photographs showing the microstructure of specimens *a*, *b*, *c*, and *d*.

4. Chemical Nonuniformity of Woods

The chemical composition of the hardwoods also differs considerably from that of the softwoods. In general the hardwoods show a lower con-



Courtesy of U. S. Forest Products Laboratory

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tent of lignin and a higher content of hemicelluloses than do the softwoods. In addition, hardwood lignin has a higher methoxyl content, and the nature of the hemicelluloses also differs. The softwoods will generally have mannan contents between 5.0 and 16.0%. The hardwoods, in contrast, contain much less mannan. Birch may have almost none whereas aspen sometimes contains up to 3.0%. The hardwoods have a much higher xylan content than do the softwoods.

Differences in the amount and nature of the wood extractives seem to be associated more with the individual species than with their classification as hardwoods or softwoods. Some woods like quebracho, chestnut, and redwood are rich in tannins; others, such as the heartwood of southern pine, contain sensible amounts of ether-soluble terpenes and fats. The heartwood of western red cedar yields interesting products of the type of thujaplicin. Conidendrin, classified as a lignan, is found in the wood of certain members of the spruce, hemlock, and fir families; spent Western hemlock sulfite liquor represents a potential source of conidendrin.

The relative amounts of the principal chemical constituents likewise are found to vary considerably among the various species of hardwoods and softwoods. Because of the complexity of wood, it is usual to employ rather conventionalized methods of analysis. Table 1 gives analyses of typical hardwoods and softwoods according to such a scheme.[1]

The total extractives represent the percentage of wood constituents removed by the successive extraction of sawdust with ether, alcohol, and hot water. The extractive-free wood sample is then treated with sodium chlorite and acetic acid under conditions as described by Wise, Murphy, and D'Addieco.[2] The residual material represents the product which can be separated into hemicelluloses and alpha-cellulose. The hemicelluloses are dissolved by treatment of the residue with 5% KOH, followed by a second extraction with 24% KOH. The alkali-insoluble portion is termed *alpha-cellulose*. It should be noted that the alpha-cellulose here defined

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[1] Data taken from the files of The Institute of Paper Chemistry.

[2] L. E. Wise, M. Murphy, and A D'Addieco, *Paper Trade J.*, **122**, 35 (Jan. 10, 1946).

Fig. 7 Blocks of wood and some of its fractions.

(*a*) Small block of wood, 3 mm on edge, freed of infiltrated substances.
(*b*) Holocellulose from *a*
(*c*) Lignin from *a*.
(*d*) Ash residue from *a*

(*a′*) Cross section of wood, *a*.
(*b′*) Cross section of holocellulose, *b*.
(*c′*) Cross section of lignin, *c*.
(*d′*) Cross section of ash residue, *d*.

Magnifications: (*a′*) ×20 diam.; (*b′*) ×100 diam.; (*c′*) ×200 diam.; (*d′*) ×50 diam.

TABLE 1. Composition of Typical Hardwoods and Softwoods[1]

	Dry basis				Extractive-free dry basis		
	Total extractives, %	Alpha-cellulose, %	Hemi-celluloses, %	Lignin, %	Mannan %	Xylan, %	Uronic anhydride, %
Hardwood							
Aspen..	4.3	51.3	21.2	18.1	—	18.4	1.12
Post oak.....	9.1	41.9	20.0	21.5	—	—	—
Quebracho..	38.0	16.1	28.1	14.8	—	—	—
Softwood							
Douglas fir....	5.9	53.8	13.3	26.7	5.4	6.2	2.8
Western hemlock	5.3	48.8	14.7	28.8	4.1	7.3	5.0
Loblolly pine....	4.4	52.6	14.6	28.3	4.7	10.1	3.8
Black spruce	4.9	49.0	16.6	26.7	8.0	10.5	4.1
Western red cedar	10.2	47.5	13.2	29.3	5.1	8.1	4.2
Redwood	23.6	35.8	9.6	31.3	—	—	—

TABLE 2. Comparative Analyses of Sapwood and Heartwood in Percentage of Original Wood (Isenberg[4])

		Extractives						
	Ash	Ether	Alcohol–benzene	Hot water	1% NaOH	Pentosans	Lignin	Cross & Bevan cellulose
Jack pine								
Sapwood	—	1.6	6.5	1.9	12.9	12.2	27.0	59.2
Heartwood	—	5.2	7.5	4.3	16.7	13.2	25.5	55.2
Western hemlock								
Sapwood	—	0.5	2.1	2.6	12.2	8.6	28.8	59.8
Heartwood	—	1.0	5.8	5.1	15.6	8.3	29.5	56.9
Big-tooth aspen								
Sapwood	0.3	1.0	2.4	3.1	—	23.3	16.3	62.7
Heartwood	0.3	1.0	2.1	1.0	—	23.8	16.9	64.4
Yellow birch								
Sapwood	0.1	0.4	1.0	1.3	—	26.9	18.6	59.4
Heartwood	0.5	0.3	1.9	1.3	—	26.9	20.2	58.4

differs from that used in the analysis of dissolving pulps (see Chapter XII-A). The material dissolving in the potassium hydroxide and precipitated by alcohol from an acid solution is *hemicellulose.* Lignin is determined on the extractive-free wood by treatment first with 72% H_2SO_4, followed by boiling 3% H_2SO_4. Under these conditions lignin is insoluble. Unfortunately, these fractions are defined by the methods of isolation; the results do not compare closely with early analyses reported in the literature because of the differences in the methods used.

The structural difference between springwood and summerwood was pointed out in an earlier section. To some degree there is also a chemical difference between these components and between sapwood and heartwood. Hägglund and Johnson[3] studied the composition of springwoods and summerwoods of spruce and found springwood to have a somewhat higher pentosan content, whereas the summerwood had a higher methoxyl content; the lignin values were almost the same.

Isenberg[4] gives a comparative analysis of sapwood and heartwood for a variety of both softwoods and hardwoods. It is difficult to identify any trends from the data other than to say that chemical differences exist. Table 2 shows analytical data for several species.

As has already been shown in the discussion of cotton cellulose (see Chapter III-B) the cellulose molecules vary in length over a wide range of degree of polymerization (D.P.). This same observation holds for wood cellulose. One condition which wood cellulose imposes to a greater degree than does cotton cellulose is the fact that in addition to differences in D.P. distribution in the natural state, conditions required for the liberation of the wood fiber, that is, pulping and bleaching, generally cause a significant degradation in the D.P. of the cellulose. The effect varies with the particular conditions and chemical agents used for both pulping and bleaching. This adds still another factor in the heterogeneity of the pulps actually used for the production of paper and for chemical conversion.

5. The Fine Structure of Wood

In order to understand the relationship between the physical structure of the wood and the location of its chemical components, it is necessary to have some knowledge of the fine structure of wood. This subject is discussed in detail in Chapter IV-C.

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[3] E Hägglund and T. Johnson, *Zellstoff u. Papier,* **7,** 49 (1927).

[4] I. H. Isenberg, "Composition of Wood," in J. N. Stephenson, editor, *Pulp and Paper Manufacture* (Preparation & Treatment of Wood Pulp, Vol. I), McGraw-Hill, New York, 1950, Chapter I, Part 2, p. 60.

The fine structural details of the fibers are sometimes altered during pulping and chemical refining. In preparing wood pulp, for example, various quantities of the middle lamella and fiber-wall lignin are dissolved and separated mechanically from wood chips. The extent to which lignin

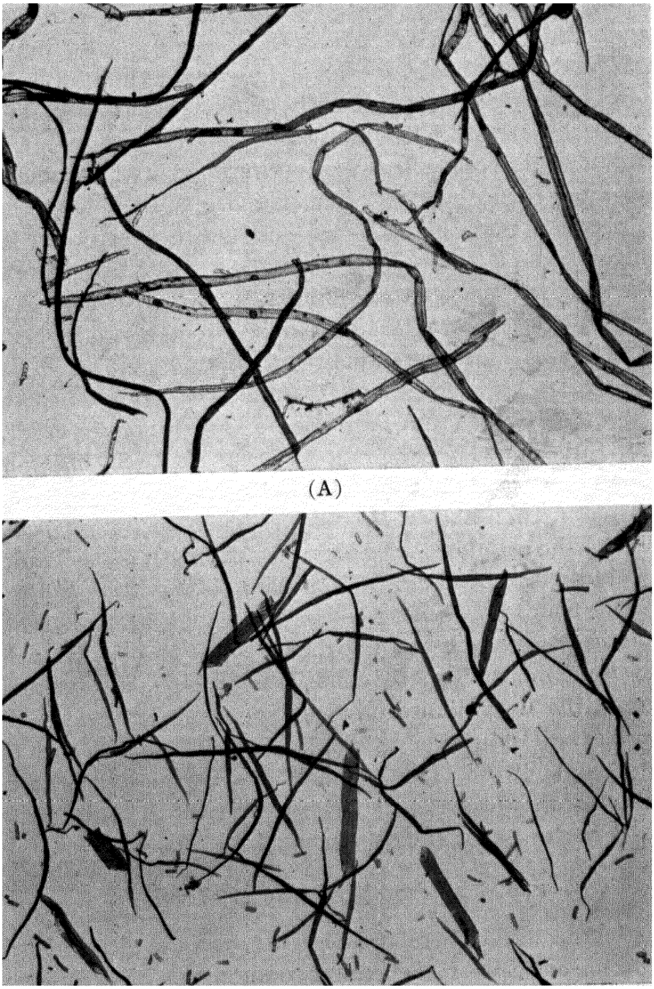

Fig. 8. (A) Jack pine kraft pulp. Magnification ×25. (B) Aspen kraft pulp. Magnification ×25.

is removed is governed by the nature of the process and the type of pulp desired. In making high-yield semichemical pulp, up to 90% of the wood may be recovered as pulp; the pulp retains most of the fiber-wall lignin and large amounts also of the middle-lamella lignin. In contrast, the full chemical pulping treatment may produce a fiber freed of much of the lignin from the middle lamella and the fiber wall. In the pulping reaction the more readily soluble portions of the hemicelluloses dissolve first. As the severity of the pulping reaction increases, lignin and hemicelluloses in increasing amounts go into solution, and even some cellulose is lost by degradation to soluble products.

The fibers of the hardwood and the tracheids of the softwood are the principal structural elements of pulps produced by the chemical pulping processes. Figure 8A shows a jack pine kraft pulp; a few small ray cells are to be seen, but the greater share of the material consists of the tracheids, known to the papermaker as fibers. Figure 8B shows a sample of an aspen kraft pulp at the same magnification. Here, in addition to the fibers, a number of larger diameter vessels are visible together with a number of small ray and parenchyma cells. The fibers and tracheids remain intact in the bleached pulp and are retained on the screen. The ray cells are much smaller than the fibers and the tracheids, and a majority of the smaller ones are lost during the mechanical handling of the pulp. Further, the ray cells contain higher percentages of readily soluble hemicelluloses which dissolve during the pulping process and thereby allow their more stable residual cellulose structure to disintegrate into fragments too small to be retained on the pulp screen.

Wide variations in fiber length, fiber width, and wall thickness are shown among the fibers in a pulp made from a single tree. As has been pointed out, fibers laid down in the spring have relatively thin walls; those laid down in the summer have thicker walls. Accordingly, pulp fibers from springwood are relatively thin-walled and twisted: the summerwood fibers are thick-walled and straight. Similarly, the average length of the fibers differs in fast-growing and slow-growing trees. Hägglund and coworkers[5] have shown that fast-growing spruce may have an average fiber length between 2.22 mm. and 3.04 mm., whereas slow-growing spruce shows an average fiber length of 3.19 mm. to 3.78 mm. In contrast, the average diameter of the fast-growing fibers exceeds that of the slow-growing fibers. The ratio of length to diameter varies between 44 and 63 for the fibers from the fast-growing wood and between 80 and 92 for those from the slow-growing wood. The length is also somewhat dependent upon the location of the

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[5] E. Hägglund and coworkers, *Svensk Papperstidn.*, **37**, 133 (1934); **38**, 454 (1935).

TABLE 3

Physical Characteristics of the Fibers and Other Elements of Selected Softwood and Hardwood Pulpwood Species (Isenberg[7])

	Average length, mm.	Spread, mm	Diameter spread, μ	% vol occupied by		
				Tracheids	Vessels	Rays
Softwood:						
Jack pine	3.5	1.5–5.7	28–40	—	0	—
Longleaf pine	4.9	—	35–45	90.8	0	8.4
Western larch	3.3	—	40–50	89.0	0	10.0
Black spruce	3.3	1.3–4.9	25–30	94.8	0	5.0
Sitka spruce	5.6	3.6–7.3	35–45	92.5	0	7.2
Douglas fir	3.9	1.7–7.0	35–45	92.5	0	7.3
Western hemlock	4.2	1.8–6.0	30–40	91.2	0	8.8
Balsam	3.5	1.9–5.6	30–40	94.3	0	5.7
Redwood	6.1	2.9–9.3	50–65	91.2	0	7.8
Hardwood:				Fibers		
Aspen	1.0	0.4–1.9	10–27	55.1	33.8	11.1
Yellow birch	1.85	0.8–2.7	20–36	65.8	21.4	10.8
Chestnut	1.0	0.5–1.7	16–34	46.8	39.8	11.9
Yellow poplar	1.9	0.8–2.7	24–40	49.2	36.6	14.2
Black gum	1.8	0.8–2.7	20–32	45.0	38.4	16.6

particular fiber in the tree. In general, fibers adjacent to the pith in coniferous trees are much shorter than are the fibers farther out in the trunk. Beyond the fiftieth year there is little change in the average fiber length. The longest fibers are found in wood at about 10 to 20 feet from the ground; above 20 feet or below 10 feet the fibers are found to be progressively shorter. One other generalization holds—namely, that wood of one species grown in colder climates has been found to show longer fiber lengths and greater fiber diameters than the same species grown in warmer climates.[6] This difference is reflected in the quality of the pulp and paper made from the two different samples.

On the average, fibers from softwoods are longer than the fibers from hardwoods. In Table 3 there have been assembled some data on the physical characteristics of pulp fibers from a number of the more important softwood and hardwood species.[7]

The relationship of fiber length, fiber diameter, and fiber wall thickness to the papermaking properties of pulps has been discussed at some length by Haywood.[8] In general, it may be said that the greater strength developed by softwood pulps is related to their greater fiber length. As a corollary, the strength of hardwood pulps is improved by removing short ray cells, thereby increasing the average fiber length. Furthermore, long-fibered pulps with large fiber diameters and relatively thick walls show fewer fibers per gram than will pulps of somewhat the same fiber length but of finer diameter and thinner cell walls. The extent of the difference may be illustrated on the one hand by sulfate pulps from Douglas fir and on the other by spruce. One sample of Douglas fir sulfate pulp had 3.5 million fibers per gram; the spruce sulfate pulp, in contrast, had 4.3 million fibers per gram. The number of fibers per unit weight is related to the amount of the bonded area in a sheet of paper and to certain of the physical properties of the paper (see Chapter VIII).

6. Variations in Pulp Fibers as a Result of the Method of Pulping

The variations thus far considered have been the fundamental differences in the structure of wood as it develops in nature. The particular method of pulping employed will develop further differences in fiber characteristics, even from the same wood source. Jayme and von Köppen[9] have discussed the structural and chemical differences between sulfite and sulfate pulps. The authors pulped sprucewood chips to approximately the same lignin content—namely, 3.58% in the case of a sulfite pulp and 3.60% in the case of a sulfate pulp. The chemical compositions of the two pulps are shown in Table 4.

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[6] H. N. Lee and J. D. Hale, "Structural, Microscopical, and Physical Characteristics of Wood," in J. N. Stephenson, editor, *Pulp and Paper Manufacture* (Preparation & Treatment of Wood Pulp, Vol. I), McGraw-Hill, New York, 1950, Chapter I, Part 1, pp. 34, 36.

[7] I. H. Isenberg, *Pulpwoods of the United States and Canada*, 2d ed., The Institute of Paper Chemistry, Appleton, Wis., 1951.

[8] G. Haywood, *Tappi*, **33**, 370 (1950).

TABLE 4. Comparison of the Chemical Compositions of a Sulfite and a Sulfate Pulp of the Same Lignin Content[9]

Component	Sulfite pulp	Sulfate pulp
Lignin	3.58%	3.60%
Carbon dioxide	0.52	0.32
Uronic anhydride	2.08	1.28
Total furfural	3.34	5.63
Furfural from uronic anhydride	0.73	0.45
Furfural from pentosan	2.61	5.18
Pentosan	3.59	7.12
Alpha-cellulose, ash-free and lignin-free	83.87	90.18
Alpha-cellulose, ash-free, after bleaching with sodium chlorite	86.60	89.90

Although the conditions in these two cooks were not those of normal commercial practice, the data serve to point up the chemical differences between sulfite pulp and sulfate pulp. These may be summarized by saying that the sulfite pulps have a higher polyuronide content and a lower pentosan content, a greater solubility of the hemicellulose constituents, and less sensitivity to sodium chlorite. One of the most interesting observations is the fact that the lignin residue in the sulfite pulps is largely concentrated in the outer wall of the pulp fibers, yielding what the authors call a skeleton which possesses a cell wall structure. The lignin content in the secondary wall of the sulfite fiber is extremely low. A very different result is found for the sulfate pulp. In this case, the lignin residue is apparently distributed rather uniformly throughout the entire fiber wall because, when the carbohydrate material is hydrolyzed by acid (as during saccharification), the isolated lignin which remains has a structureless amorphous character.

The preceding section has covered to some degree the variations in pulp fibers which are reflected in paper quality. It should be pointed out, however, that these do not represent all of the differences in fibers from various sources. Some of these undetermined differences may have a greater influence on the properties of the paper than do the ones already listed. Among the other properties of fibers which affect the physical properties of a sheet of paper are the orientation of the cellulose molecules in the fiber wall, the relative amounts of so-called accessible and nonaccessible cellulose, the relative sizes of the accessible and nonaccessible parts of the fiber, the amount of specific surface either directly or potentially available, and the relative locations of different types of hemicelluloses and other chemical constituents in the fiber. In addition to these, there are probably still a number of other important variables in either structure or composition which so far have escaped identification and measurement. As long as this condition holds, it is not possible for the papermaker to develop any kind of physical measurement or chemical analysis of a sample of pulp and to predict therefrom with any assurance the physical properties of the sheet made from that pulp. As a result, the pulp and paper technologist still depends upon the miniature beater and the formation of standard handsheets of paper for evaluating the quality of a pulp—a process which is empirical and often almost nonreproducible because of differences in testers and testing equipment.

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[9] G. Jayme and A. von Köppen, *Das Papier*, **4**, 373, 415, 455 (1950).

7. Chemical Modification of Wood

Modification of the properties of wood is sometimes desirable for special uses; methods used are various impregnation treatments, compression, or both. One of the chief improvements sought is dimensional stability. This has been accomplished to varying degrees in five different ways: (1) coating the external or internal surface of the wood with water-insoluble materials to retard the rate of moisture loss or gain; (2) heating wood to elevated temperatures for short periods of time; (3) depositing within the cell walls bulking agents that block the normal shrinkage; (4) replacing by chemical means the hygroscopic hydroxyl groups of cellulose and lignin with less hygroscopic goups; (5) forming chemical cross bridges between structural units.

The first method is of limited value as it merely retards the rate of swelling. The second is the cheapest means for obtaining permanent dimensional stability, but, unfortunately, it degrades the wood excessively for most uses. Methods 3 and 4 operate together in the most successful process; treatment of the wood with phenolic resin-forming materials that are polymerized in place within the cell wall and vapor-phase acetylation of the wood. The only successful cross-linking agent (method 5) that has been found to date, the vapor treatment with formaldehyde, requires such high acidity that the wood is badly degraded.

Resin-treated woods, especially in the compressed ("compreg") form, have found a number of industrial and military uses.[10] Resin treatment alone improves only the compressive strength properties of wood, but when the wood is also compressed prior to setting of the resin, most of the strength properties are improved in proportion to the degree of compression, with the exception of toughness which is slightly decreased.

When wood is compressed under heat and pressure without previous resin treatment, it has good strength properties and is tougher than that produced by the compreg process. Unfortunately, the wood tends to lose its compression under moist conditions. When the wood is compressed at moisture contents and high temperatures adequate to plasticize the lignin slightly (about 8% moisture content and 350°F.), internal stresses are relieved within the wood sufficiently to avoid springback.[11] This material, known as "staypak," has not yet found commercial use in the United States.

The following sections of this chapter will cover rather thoroughly the nature of the hemicelluloses and lignin in wood. In addition, the main extractives will be reviewed.

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[10] A. J. Stamm, in *Modern Plastics Encyclopedia, 1948*, Plastics Catalogue Corp., New York, 1948, p. 725; A. J. Stamm and R. M. Seborg, U. S. Forest Products Laboratory, Mimeographed Report **1381** (Revised 1949).

[11] R. M. Seborg, M. A. Millett, and A. J. Stamm, *Mech. Eng.*, **67**, 25 (1945).

B. NONCELLULOSIC CARBOHYDRATES[1]

A. G. NORMAN

1. Sugars Found in Hemicelluloses and Related Polysaccharides

The photosynthetic process in the green plant results in the production of a hexose phosphate, probably by reactions that are the reverse of those encountered in normal glycolysis. Glucose appears as the building unit of the two polysaccharides that have major roles in the plant, namely, cellulose as a structural constituent, and starch as a reserve. However, other polysaccharides associated with cellulose in the cell wall or, like starch, present in the cell may contain or be exclusively composed of sugar units other than glucose. Conversion of one hexose into another is presumably easily accomplished in the plant, though of the 24 possible aldo- and keto-hexoses, only five are known to occur naturally in plants. These are D-glucose, D-fructose, D-mannose, D-galactose, and L-galactose, the last being very rare. The transformation from the normal form of glucose to mannose or galactose involves a transposition of OH and H groups on carbon atom 2 or 4. Neither D-mannose nor D-galactose has been identified in the free condition in plant tissues which suggests that the transformation occurs at the time of polysaccharide synthesis or, far less probably, when the sugar is linked in a polysaccharide condition.

Pentose and hexuronic units also are common in polysaccharides of plant origin. Their formation from hexoses is inferred, though there is no good evidence disproving their direct formation in the chain of reactions involved in photosynthesis. Of the possible aldohexuronic acids and pentoses only three of the former and two of the latter seem to occur in plant polysaccharides. These are D-glucuronic acid, D-galacturonic acid, D-mannuronic acid (the last only in certain marine algae), D-xylose, and L-arabinose. It will be seen (Fig. 9) that configurationally these are directly related to the three aldohexoses mentioned above. Two series seem to be complete, namely, the glucose-glucuronic-xylose series and the galactose–galacturonic-arabinose series. It is perhaps of significance that in some polysaccharides these sterically related sugars are present together as constituent units.

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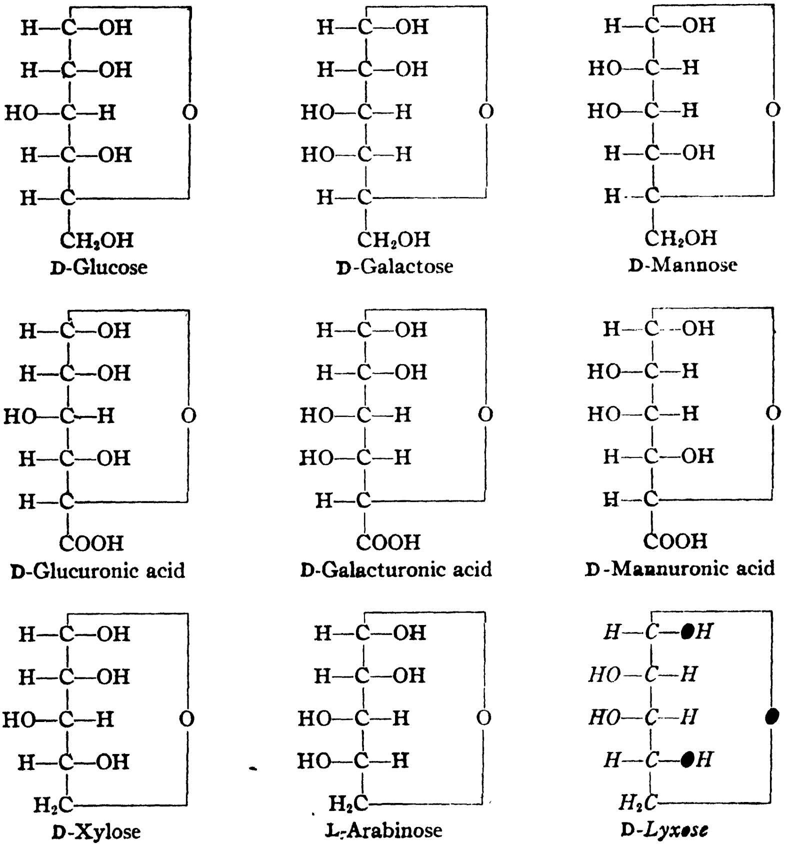
[1] An extended treatment of the relationship between hemicelluloses and other cell wall constituents is to be found in A. G. Norman, *The Biochemistry of Cellulose, the Polyuronides, Lignin, etc.*, Clarendon Press, Oxford, 1937; and more recently in R. L. Whistler and C. L. Smart, *Polysaccharide Chemistry*, Academic Press, New York, 1953



D-Glucose D-Galactose D-Mannose

D-Glucuronic acid D-Galacturonic acid D-Mannuronic acid

D-Xylose L-Arabinose D-*Lyxose*

Fig. 9. Configurational relationships of sugars found as constituent units in plant cell-wall polysaccharides.

For example, hemicelluloses have been isolated containing glucose, glucuronic, and xylose groups, the last predominating. Pectin appears to be a polygalacturonide, but is usually associated with araban and galactan. Water-soluble arabogalactans are present in larch wood. Such observations make plausible the theory of a hexosan→hexuronide→pentosan transformation, though the evidence for such is no more than presumptive. The mannose series is incomplete in that the corresponding pentose, D-lyxose, is unknown, and the uronic acid of the series, D-mannuronic acid, has been found only in the polysaccharide, alginic acid, isolated from certain marine algae. In plants containing mannan, such as conifers, no mannuronic acid has ever been identified.

Available information on the biosynthesis of polysaccharides suggests that formation from phosphorylated sugar units is most probable. This would mean that a pentosan is more likely to arise by direct synthesis than by the *in situ* oxidation and decarboxylation of a hexosan. It must be admitted that sterically the latter might be possible and that mixed polysaccharides containing hexose, hexuronic, and pentose groups might be obtained in this way, but the evidence in support of such transformations is frail.

2. Hemicelluloses

(a) DEFINITION

The cellulosic fabric in the primary and secondary cell walls of plants forms a continuous system, which is, however, porous or spongelike with communicating interstices. In these elongated spaces are deposited the amorphous cell-wall constituents, mainly lignin and polysaccharides that are described as hemicelluloses. These noncellulosic unoriented components similarly form a more or less continuous interpenetrating system and no doubt have a stiffening effect on the wall as a whole. The three major constituents of the mature cell wall, namely, cellulose, hemicelluloses, and lignin, are therefore in the closest physical association, and inasmuch as some of their chemical properties overlap, sharp separation is a matter of considerable difficulty. The distinction between cellulose and hemicelluloses was made first by Schulze[2] on the basis of the solubility of the latter in dilute alkalies. It was his belief, however, that the hemicelluloses were closely related to cellulose both chemically and functionally, hence the similarity in nomenclature.

Definitions based largely on properties are rarely wholly satisfactory, yet even now it is not possible to provide an alternative which entirely omits properties. In its present usage the term hemicelluloses includes those cell-wall polysaccharides which are removable from the untreated tissues by extraction with cold or hot alkali, and which may be hydrolyzed by boiling with dilute acids to give constituent monosaccharide units. More than one sugar may be found on hydrolysis, and hexuronic groups may also be present. This definition of the hemicelluloses causes to be included together polysaccharides of at least two types with perhaps different roles and from different locations in the cell wall. There is no doubt that an attempt should be made to distinguish between these two types of polysaccharides in all chemical studies on plant materials, even though it may not be possible to separate them in an alkaline extract. Under the general title of hemicelluloses there are included, therefore, those amorphous polysaccharides that form a part of the system which interpenetrates and incrusts the cellulosic fabric, and also those short-chain polysaccharides that form a part of the cellulosic fabric itself. Until extracted, the latter exist only in association with cellulose and *in situ* are oriented in the micellar structure.

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[2] E. Schulze, *Ber.*, 24, 2277 (1891).

Representatives of these two groups exhibit certain chemical differences. Uronic groups seem to be characteristically present in the incrusting polysaccharides and for this reason they are sometimes referred to as "polyuronide hemicelluloses." Only glucuronic and galacturonic acids have been authentically reported. The accompanying sugar units may be either hexoses or pentoses or both. Evidence has been presented in support of the view that the polyuronide hemicelluloses may at least in part be linked to lignin, though it is by no means certain that this is invariably or exclusively the case.

The study of the polyuronide hemicelluloses has been much hampered by the fact that preparations have also contained polysaccharides concurrently extracted from the cellulose. These have been termed "cellulosans" and do not characteristically contain hexuronic units, although some carboxyl groups of this type may be present. On hydrolysis, one or at most two sugars are obtained. The cellulosans, therefore, seem to be relatively simple hexosans or pentosans that *in situ* were to some degree oriented in the micellar cellulose fabric. The cellulosan fraction of angiosperm plants usually seems to be predominantly a xylan, though there may be present also some glucan that probably represents very short cellulose chains. The cellulose of gymnosperms (softwoods) has usually a considerably lower xylan content and, in addition to the glucan just referred to, it also contains a mannan. The study of the cellulosans is far less difficult than that of the polyuronide hemicelluloses because they may be obtained directly in a relatively pure condition by the alkaline extraction of cellulose prepared by the chlorination procedure that is the basis of the Cross and Bevan method (see Chapter XII-A) for the determination of cellulose. They form in the main that indefinite fraction of pulps known industrially as beta- and gamma-cellulose.

Exception has been taken to the term cellulosan by several workers,[2a-b] primarily on nomenclatural grounds, in that it attaches to the name of a polysaccharide an ending ordinarily employed for designating anhydro sugars. Others, although recognizing the fact that the noncellulosic cell-wall polysaccharides are far from uniform, have not accepted the term because they are unwilling to accept the distinction made in the second and third paragraphs of this section. In general this arises from different views as to what constitutes cellulose, and whether alpha-cellulose, the product of an arbitrary extraction procedure, is tacitly assumed to consist only of the long-chain anhydroglucose units that form the classical concept of the cellulose molecule. For the present, however, the term cellulosan is useful in that it describes in one word some cell-wall polysaccharides that could only otherwise be designated in an involved circumlocution.

(b) DETERMINATION AND OCCURRENCE

The relationships between the major cell-wall constituents as outlined above are indicated, highly diagrammatically, in Figure 10. The separation of the hemicelluloses into two groups, (1) the cellulosans and (2) the polyuronide hemicelluloses, rests primarily on the Cross and Bevan cellulose method which involves the use of neutral reagents only. It cannot be said that separation between these two groups can be sharply effected, because chemical or physical pretreatments affect the recoveries of the two types.[3-6] Moreover, if a different delignification procedure is followed such as that resulting in the isolation of the holocellulose fraction (see Section A of this Chapter V) the distinction between the cellulosan and the noncellulose-associated hemicelluloses is more difficult to perceive because their physical and solubility properties are so similar. The delignification process should not affect the association between cellulosans and cellulose, but the incrusting polyuronide hemicellulose fraction is rendered distinctly more soluble thereby.

For various reasons, it is not possible to give accurate figures for the total

[2a] R. L. Whistler, *Advances in Carbohydrate Chemistry*, **5**, 270 (1950).

[2b] R. L. Whistler and C. L. Smart, *Polysaccharide Chemistry*, Academic Press, New York, 1953.

[3] W. G. Campbell and J. Booth, *Biochem. J.*, **24**, 641 (1930).

[4] A. W. Mackney, *J. Council Sci. Ind. Research*, **13**, 115 (1940).

[5] L. E. Wise, F. C. Peterson, and W. M. Harlow, *Ind. Eng. Chem., Anal. Ed.*, **11**, 18 (1939).

[6] J. D. Reid, G. H. Nelson, and S. I. Aronovsky, *Ind. Eng. Chem., Anal. Ed.*, **12**, 255 (1940).

amount of hemicelluloses present in plant materials. There is no simple extraction method which will remove quantitatively all hemicelluloses without affecting other constituents, nor is it easy to see how any simple method can be devised to determine polysaccharides with more than one constituent sugar. Several procedures involving dilute acid hydrolysis and titration of reducing groups have been proposed but none is wholly satisfactory. The hydrolytic treatment fails to separate the cellulosans from the incrusting polyuronide hemicelluloses, but for some purposes this may be an unimportant objection. More serious is the fact that the hydrolysis of the polyuronide hemicelluloses does not proceed smoothly to completion. Resistant aldobiuronic acids may be present which will survive boiling for many hours. Liberated uronic acids, however, are decarboxylated under such conditions, and pentose sugars are slowly destroyed. Complete recoveries of reducing sugars from hemicelluloses are, therefore, not obtained. A combination of hydrolytic and fermentation methods has been employed with a greater degree of success.[7]

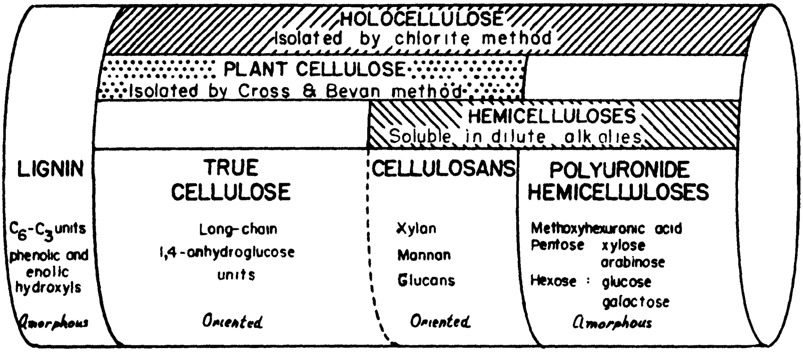
HOLOCELLULOSE
Isolated by chlorite method
PLANT CELLULOSE
Isolated by Cross & Bevan method
HEMICELLULOSES
Soluble in dilute alkalies
LIGNIN
C6-C3 units
phenolic and enolic hydroxyls
Amorphous
TRUE CELLULOSE
Long-chain 1,4-anhydroglucose units
Oriented
CELLULOSANS
Xylan
Mannan
Glucans
Oriented
POLYURONIDE HEMICELLULOSES
Methoxyhexuronic acid
Pentose xylose
arabinose
Hexose : glucose
galactose
Amorphous

Fig. 10. Diagram illustrating relationships between major cell-wall constituents.

Dilute acid hydrolysis of straw holocellulose has been said to yield a residue quantitatively equal to the Cross and Bevan cellulose[8] and by difference a figure for the polyuronide hemicellulose content.

Both Preece[9] and Buston[10,11] have attempted hemicellulose determination by isolating the polysaccharides quantitatively on a small scale. The procedure is tedious and applicable only to special problems. Corrections have to be applied for lignin, protein, and ash, some of each of which may be present in the preparations. These preparations, of course, include both cellulosans and polyuronide hemicelluloses, and the complete picture is not obtained unless the residue is examined also.

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[7] A. H. Auernheimer, L. J. Wickerham, and L. E. Schniepp, *Anal. Chem.*, **20**, 876 (1948).

[8] G. A. Adams and A. E. Castagne, *Can. J. Research*, **27B**, 907 (1949).

[9] I. A. Preece, *Biochem. J.*, **25**, 1304 (1931).

[10] H. W. Buston, *Biochem. J.*, **28**, 1028 (1934).

[11] H. W. Buston, *Biochem. J.*, **29**, 196 (1935).

An alternative and somewhat simpler approach involves isolation of the holocellulose fraction, which is then exhaustively extracted with dilute alkali. The hemicellulose content is determined either by difference[12] or by direct precipitation with alcohol from the combined alkaline extracts.[13] A simple proximate procedure suggested by Bennett[14] involves extraction of the hemicelluloses from the holocellulose fraction followed by acid chromate oxidation of the extract.

The most satisfactory approach to the problem of hemicellulose determination lies perhaps in separate analyses for particular groups known to be present, and this in fact is the method commonly employed in plant analysis. Under certain circumstances the figures so obtained may not be far short of the actual totals. The total pentose content of the material and that of the Cross and Bevan cellulose isolated therefrom are separately ascertained, thus giving by difference the pentose groups in the polyuronide hemicellulose fraction. Uronic determinations may also be carried out, preferably after extraction with 0.5% ammonium oxalate to remove pectic substances. These three determinations are sufficient to characterize many mature materials, inasmuch as the polyuronide hemicelluloses are frequently xylan–glucuronides with xylose units predominating and the cellulosan similarly is predominantly a xylan. In softwoods, mannan may be present with xylan in the cellulosan fraction and this can be determined with a fair degree of accuracy.[15,16] Hexose units such as glucose or galactose in the polyuronide hemicelluloses are at present undeterminable. Glucose is rarely an important constituent but galactose may be a major constituent in hemicelluloses of the galactan–araban–galacturonide type, which are more frequently found in green unlignified tissues.

In general, it seems that the total hemicellulose content of plant materials falls within the range of 10 to 30%, and, of that present, as much as one-half may be cellulosan. The relationship between polyuronide hemicelluloses and cellulosans is by no means a constant one during development and maturation of a tissue, although there is not usually any pronounced or greatly disproportionate change.

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[12] L. E. Wise and E. K. Ratliff, *Anal. Chem.*, **19**, 459 (1947).

[13] H. D. Weihe and M. Phillips, *J. Agr. Research*, **74**, 77 (1947).

[14] E. Bennett, *Anal. Chem.*, **20**, 642 (1948).

[15] A. Nowotnowna, *Biochem. J.*, **30**, 2177 (1936).

[16] L. E. Wise, E. K. Ratliff, and B. L. Browning, *Anal. Chem.*, **20**, 825 (1948).

3. Relationship between Hemicelluloses and Other Cell-Wall Constituents

(a) POLYURONIDE HEMICELLULOSES

The behavior of the polyuronide hemicelluloses in respect to extracting agents cannot be explained without assuming linkage to some other cell-wall constituent, probably lignin (see Section C of this Chapter V). Some variation in solubility would be expected if polysaccharides of different chain length or different degrees of molecular aggregation were present, but this is insufficient to account for the fact that the polyuronide hemicelluloses cannot be extensively or completely removed from lignified tissues without the application of a treatment that might dissociate a linkage with lignin. Similarly, lignin cannot be removed without simultaneous liberation or decomposition of these polysaccharides. The lignin–polyuronide hemicellulose complex cannot be separated unchanged for direct study, though the isolation of a small amount of a lignin–carbohydrate compound has been reported.[17] A glycosidic linkage is probably involved,[18] but it is most unlikely that the combining power of the one component for the other component is satisfied at all times. Moreover, the homogeneity of lignin is by no means assured.[19] The form of association between lignin and hemicelluloses is therefore likely to be complex. This is fully in line with observations on the extraction of the latter with alkali which brings about solution of the hemicelluloses to an extent depending on the concentration, temperature, and time. The extent of extraction by cold alkali is much increased if preceded by chlorination, and this fact has been utilized in preparational work.

Further evidence for the existence of a lignin-hemicellulose linkage has been obtained by following the removal of hemicelluloses during the isolation of Cross and Bevan cellulose.[20] Hemicelluloses pass into solution in sodium sulfite along with the lignin only if the sulfite treatment is preceded by chlorination. To a considerable extent they are even soluble in water after chlorination, which presumably brings about rupture of the linkage with lignin. Similarly, from tissues that have been completely delignified by one of the methods for isolation of the holocellulose fraction, the ease of extraction of polyuronide hemicelluloses is greatly increased. However, even then they are not of uniform and equal solubility. Some hemicelluloses may be extracted readily with water, but dilute alkali is still necessary to effect solution of the main fraction.[21,22] Swelling evidence supports the same conclusion.[23,24]

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[17] F. E. Brauns and D. S. Brown, *Ind. Eng. Chem.*, **30**, 779 (1938).

[18] K. Freudenberg, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 34 (1938).

[19] A. von Wacek and D. Schroth, *Monatsh.*, **81**, 1151 (1950).

[20] A. G. Norman and J. G. Shrikhande, *Biochem. J.*, **29**, 2259 (1935).

(b) CELLULOSANS

The form of association of the cellulosans with the cellulose is of an entirely different character and has not, in fact, been exhaustively studied. That there is no real line of separation between cellulosans and true cellulose is almost certain. The distinction is made primarily on solubility or insolubility in dilute alkali, and susceptibility or resistance to hydrolysis by dilute acid. The separation that is made is purely arbitrary and varies with the concentration, temperature, and length of treatment with the reagent. For example, the conventional procedure for obtaining alpha-cellulose does not invariably yield a product that consists only of true cellulose molecules. Furthermore alpha-cellulose preparations even after prolonged hydrolysis with dilute mineral acids may still contain sugar units other than glucose. Pentose units were shown to be present in hydrolyzed preparations from oak cellulose,[24a] and mannose in hydrolyzed alpha-cellulose from slash pine[24b] and aspen.[24c] Jute cellulose has been studied in this connection with conflicting results.[24d-e]

The cellulosans associated with the true cellulose in the cellulosic fabric are believed to be relatively short-chain compounds, the xylose, mannose, or glucose units of which have a pyranose structure, and which therefore occupy longitudinally the same space as the anhydroglucose units in the cellulose chains. These short-chain polysaccharides would therefore pack readily into the oriented cellulosic structure, the longitudinal strength of which is due to the presence of immensely long cellulose chains, between which some cross-bridging or looping may also occur. The short-chain cellulosans would be retained by such lateral forces as are operative be-

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[21] R. L. Mitchell and G. J. Ritter, *J. Am. Chem. Soc.*, **62**, 1958 (1940).

[22] S. C. Rogers, R. L. Mitchell, and G. J. Ritter, *Anal. Chem.*, **19**, 1029 (1947).

[23] M. K. Sen and P. H. Hermans, *Rec. trav. chim.*, **68**, 1079 (1949).

[24] J. Larinkari, *Finnish Paper Timber J.*, **28**, No. 7A, 55 (1946).

[24a] A. G. Norman, *Biochem. J*, **30**, 2054 (1936).

[24b] L. E. Wise and E. K. Ratliff, *Archiv. Biochem.*, **19**, 292 (1948).

[24c] L. E. Wise, E. K. Ratliff, and B. L. Browning, *Anal. Chem.*, **20**, 825 (1948).

[24d] D. B. Das, M. K. Mitra, and J. F. Wareham, *Nature*, **171**, 613 (1953).

[24e] A. K. Mazumdar and P B. Sarkar, *Nature*, **172**, 1047 (1953).

tween adjacent cellulose chains. The xylan chain would lack the projecting carbinol unit of carbon atom 6, but this does not appear to affect retention appreciably, since from softwood cellulose the xylan is not removable by alkali any more readily than the mannan.[25] Examination of the x-ray diagrams obtained from fibers before and after removal of cellulosan has shown a slight improvement in orientation, but no marked change.[26,27] It is perhaps significant that the fibers of high tensile strength are those in which the cellulosan content is low. Cotton, ramie, flax, and hemp are almost free of cellulosan, whereas jute, sisal, Manila hemp (abacá), and coir all contain substantial amounts. The general architecture of the cellulose structure in the latter would be far less homogeneous and less uniform than that of the former because of the presence of the short-chain cellulosans.

The degree of crystallinity of cellulose from different sources varies greatly, reflecting in part the content of short-chain cellulosan. Optical methods[28,29] and chemical procedures based on the liberation of carbon dioxide on hydrolytic–oxidative treatment with boiling hydrochloric acid-ferric chloride mixtures[30,31] have been used to determine the percentage of crystalline cellulose.

4. Isolation and Fractionation

In investigating the hemicelluloses of plant material, most workers have wished to study the polyuronide hemicelluloses, not the cellulosans, and have worked up alkali extracts without having in mind the dual source of the polysaccharides actually present in them. Moreover, in many cases no attempt has been made to bring about complete or extensive extraction, though the fraction obtained has been regarded as being typical of the group as a whole. These errors would have been avoided had adequate analyses been made of the plant material before and after extraction, and this should be regarded as an essential step in any preparational work. Under certain conditions of extraction, the amount of cellulosan present in the extract may be small in comparison to the polyuronide hemicellulose, but the procedures used by some have certainly produced the opposite effect. Alkalies alone do not provide the best means of resolving the lignin–polyuronide hemicellulose linkage, and although the application of hot, relatively strong, alkaline solutions, often for many hours, may give a high yield of total polysaccharides, the contribution by the cellulosans will be at the maximum. That hemicellulose extracts are mixtures of two groups of polysaccharides of different origin would not be of consequence if they were subsequently easily separable. This, however, is not at present the case, though various fractionation procedures have been proposed, some of which will be discussed later.

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[25] A. G. Norman, unpublished work.

[26] W. T. Astbury, R. D. Preston, and A. G. Norman, *Nature*, **136**, 391 (1935).

[27] R. D. Preston and A. Allsopp, *Biodynamica*, No. **53**, 8 pp. (1939).

[28] R. D. Preston and M. Middlebrook, *J. Textile Inst.*, **40**, 1715 (1949).

[29] P. H. Hermans, *Makromol. Chem.*, **6**, 25 (1951).

[30] R. F. Nickerson, *Ind. Eng. Chem.*, **34**, 1480 (1942).

[31] J. F. Saeman, *Ind. Eng. Chem.*, **37**, 43 (1945).

Basically there are two general procedures that have been followed, the classical one of direct alkaline extraction and the more recent one which involves prior preparation of the delignified holocellulose fraction, and subsequent extraction. In general, higher yields are obtained by the latter procedure, which is probably to be preferred on several grounds, though it cannot be said that its proponents have supported their selection of the procedure by analyses of the preparations and residues. There is no record of a direct comparison of preparations made by the two general procedures outlined above.

In either case it has been customary to employ an exhaustive pretreatment with alcohol–benzene in a continuous extractor for many hours to remove lipides, and extractives that may be present in certain woods. The residue, after washing with alcohol and drying, is treated with warm water for several hours and then is extracted with 0.5% ammonium oxalate to remove pectic constituents. This last step may be important when immature tissues are under study, but is sometimes omitted if the pectin content is quite low.

When the ultimate extraction of the hemicelluloses has been accomplished with alkali without prior delignification, the dried pectin-free residue has next been treated with alcoholic sodium hydroxide (usually 1% NaOH in 50% ethanol) with the intention of lowering the lignin content, and so reducing the amount that passes into solution along with the hemicelluloses on subsequent extraction with alkali.[32] At boiling temperatures, however, it has been shown that a more or less serious degradative effect on the polyuronides may occur;[33–35] on the other hand, if the extraction is carried out at room temperature little removal of lignin is effected. The presence of pentose and uronide material may not be detected in the extracts, and the magnitude of the losses brought about by alcoholic sodium hydroxide can

[32] F. W. Norris and I. A. Preece, *Biochem. J.*, **24**, 59 (1930).

[33] A. G. Norman, *Biochem. J.*, **29**, 945 (1935).

[34] I. A. Preece, *Biochem. J.*, **34**, 251 (1940); **35**, 659 (1941).

[35] H. D. Weihe and M. Phillips, *J. Agr. Research*, **72**, 163 (1946).

be ascertained only by analysis of the residue. This step is therefore of dubious value.

The dried residue from the previous treatment has then been extracted several times at room temperature with 4 to 5% NaOH, and the hemicelluloses have been precipitated from the combined extracts by means described below. Sodium hydroxide in the cold, however, does not bring about solution of all the alkali-soluble polysaccharides, and accordingly various workers have treated the residue further. Some have continued alkali treatment using boiling 4% NaOH, whereas others have increased the strength of alkali. Unless the alkaline treatment is quite drastic, the residue may still contain pentose and uronic units. Alternatively, delignification by exposure to chlorine gas followed by extraction with cold 10% NH_4OH may make the residual hemicellulose fraction more easily soluble in cold alkali.[36] The ammonia treatment may be omitted and direct re-extraction with cold alkali of the same concentration as initially employed may be adopted.[37]

A simplified procedure, involving initial treatment of the material with aqueous 20% KOH for 2 hrs. at 65–70°C. followed by dilution with approximately seven volumes of water and further heating at the same temperature for 2 hrs., was found to yield a substantial fraction of the hemicelluloses. A further fraction could be obtained by alkali of this concentration only after delignification with chlorite.[22]

The hemicelluloses may be precipitated from the several extracts by acidification and addition of excess ethanol, but it has been customary at this point to commence fractionation. Separation into two or more fractions may be accomplished by differential precipitation. However, there are no sound criteria that may be applied to determine the homogeneity of fractions so obtained, and different workers have adopted a variety of fractionation methods. The main separation has commonly been made by taking off first a fraction precipitated by the simple addition of acid to the alkaline extract. This, following the nomenclature introduced by O'Dwyer,[38] has been termed hemicellulose A. Some attention has to be paid to the precise conditions of precipitation since it appears that the pH at which maximum yield is obtained varies somewhat with the source of the sample.[39] Excess glacial acetic acid has sometimes been employed but, because of the buffering effect of the sodium acetate present, this may not give a low enough pH.

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[36] E. Anderson, M. Seeley, W. T. Stewart, J. C. Redd, and D. Westerbeke, *J. Biol. Chem.*, **135**, 189 (1940).

[37] A. G. Norman, *Biochem. J.*, **31**, 1579 (1937).

[38] M. H. O'Dwyer, *Biochem. J.*, **20**, 656 (1926).

[39] S. Angell and F. W. Norris, *Biochem. J.*, **30**, 2155 (1936).

A fraction described by O'Dwyer as hemicellulose B is obtained by the addition of alcohol or acetone to the filtrate from hemicellulose A. Other workers have carried out a two-step separation at this stage, taking off fraction B first by the addition of half a volume of acetone or ethyl alcohol to the filtrate from A, and then fraction C by the addition of additional acetone or ethyl alcohol to the filtrate from B. Each fraction may be redissolved and reprecipitated several times, and further separation may be effected if desired by use of the Salkowski reaction with copper compounds.[40] A mixture of glycerol and cupric sulfate has been said to be more effective than Fehling solution.

The fraction system described above has been fairly widely employed, yet sufficient variations have been introduced so that without checking details of procedure it cannot be assumed that the B fraction of one worker was obtained in a manner identical to that used by another in obtaining a similarly described fraction. The entire absence of certain fractions from some materials has frequently been reported, but it must be borne in mind that these designations really indicate particular methods of precipitation only and not necessarily well-defined classes of hemicelluloses.

Anderson and coworkers[41] distinguished only between the "less-soluble" and "more-soluble" portions of the hemicelluloses, and kept separate the polysaccharides removed from the wood by direct extraction with alkali and the polysaccharides coming into solution only after chlorination. Four fractions were thus obtained; A and C in their system being "less-soluble" and therefore precipitated by the addition of half a volume of alcohol to the acidified extract before and after chlorination, respectively; B and D being "more-soluble" and therefore only precipitated by the further addition of three volumes of alcohol to the filtrates from A and C.

Inasmuch as lignin is soluble to some extent in alkali and is precipitated on acidification, hemicellulose preparations are apt to contain several per cent of lignin unless special precautions are adopted for its removal. Solution in alkali and reprecipitation several times with ethanol is fairly effective, since the lignin then remains in solution in the alkaline alcohol. An alternative method of removal is brief chlorination followed by precipitation with alcohol and repeated washing with 50–60% ethanol. One of the delignifying procedures devised for the isolation of holocellulose has been employed by Weihe and Phillips[42] for the removal of lignin from hemicellulose preparations. The precipitated hemicellulose is suspended and partially dispersed in a small volume of water. Chlorine is passed in slowly for 1 hr. and then excess ethyl alcohol is added. The precipitate is treated twice with a 3% solution of ethanolamine in 95% ethanol at 80°C. for 10 min. This procedure appears to be very effective in giving a product virtually free of lignin.

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[40] E. Salkowski, *Z. physiol. Chem.*, **34**, 162 (1901).

[41] E. Anderson, J. Kesselman, and E. C. Bennett, *J. Biol. Chem.*, **140**, **563** (1941)

When lignin-free holocellulose is used as the starting material for hemicellulose extraction, the procedure is not greatly different. Because the removal of the polyuronide hemicellulose fraction from such material no longer depends on the rupture of a lignin linkage, these polysaccharides are more easily soluble. The delignification process should not affect the association between cellulosans and cellulose so that no change would be expected in the properties of that group. The consensus of opinion is that the treatments involved in the isolation of the holocellulose fraction do not result in an appreciable loss or modification of polysaccharides. This appears to be well established for some hardwoods but is less well assured in the case of some softwoods[43] and straws.[44] Alkaline extraction is necessary to put into solution the major portion of the hemicelluloses in a holocellulose preparation, so that the polysaccharides present are still likely to be of dual origin. However, a water-soluble fraction, which would probably not be contaminated with cellulosan, can be obtained, and much of the alkali-soluble material can be taken off by mild methods that would not produce so extensive an attack on the cellulosans as ordinarily occurs. For example, a sequence of extractions with (a) water at 95°C. for 1 hr., (b) 2% sodium carbonate at 20°C. for 24 hrs., and (c) 4% NaOH at 20°C. for 24 hrs. yielded the major part of the hemicelluloses present in maple holocellulose.[45]

The preparation of cellulosans in a pure condition is a matter of no great difficulty. The starting material in this case is the cellulose fraction isolated from the plant material by the Cross and Bevan method or one of its modifications. For laboratory-scale preparations, chlorination by hypochlorite may be substituted for chlorination by chlorine gas. Pulps obtained by ordinary commercial pulping methods may also be employed, though it must be remembered that some loss of cellulosan has already occurred by hydrolysis. The cellulosan may be extracted by treatment with hot alkali; the amount removed will depend on the time and temperature of treatment. Purification can be carried out by precipitation with copper as described above. Celluloses from sources other than softwoods have been found to yield xylans; the earlier structural work on xylan was in fact carried out on material extracted from esparto pulp. Preparations from softwood celluloses also contain mannan. In a study of unbleached kraft pulps from western hemlock and Douglas fir it was found that all of the mannan but only about one-third of the xylan was associated with the alpha-cellulose.[16]

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[42] H. D. Weihe and M. Phillips, *J. Agr. Research*, **60**, 781 (1940).

[43] C. V. Holmberg and E. C. Jahn, *Paper Trade J.*, **111**, 33 (July 4, 1940).

[44] G. A. Adams and A. E. Castagne, *Can. J. Research*, **26B**, 325 (1948).

[45] R. L. Mitchell, S. C. Rogers, and G. J. Ritter, *Ind Eng. Chem* , **40**, 1528 (1948).

5. Composition and Structure

The constitutional chemistry of the hemicelluloses, particularly the polyuronide hemicelluloses, is in an unsatisfactory state, though procedures have now been developed that may result in early clarification. Probably the best that can be said at this time is that there is some general information as to the nature of the constituent groups involved in hemicelluloses from a considerable number of different sources. It is likely that all hemicellulose preparations so far obtained have been mixtures, but there is, in fact, reason for believing that the methods of separation and fractionation that have been rather generally used may have given a spuriously complex picture. Differential precipitation does not necessarily accomplish separation into chemically distinct entities. The major separation ordinarily employed in one form or another distinguishes only between the less-soluble and more-soluble fractions. Hemicellulose A preparations represent those polysaccharides easily precipitated, and B and/or C preparations consist of those fractions that are presumably of smaller molecular dimensions and which require the addition of alcohol or acetone for their precipitation. Polysaccharides usually have a chain structure, but there is the possibility that one polysaccharide existing as molecules of different chain length could appear in all fractions. Similarly, if the polysaccharide had a branched chain like some of the plant gums, separation by physical means might again give fractions that did not differ with respect to the amounts of the several components present. It is likely, therefore, that the system of differential precipitation will give chemically distinct fractions only if it happens that these differences are also clearly correlated with differences in molecular size. In general, the more-soluble fractions appear to have a higher uronic content than the less-soluble

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[46] H. F. Lewis, L. E. Wise, and B. L. Browning, *Tappi*, **33**, 92 (1950).

fractions. For example, the contents of methoxyhexuronic acid in the most-soluble and least-soluble fractions from black locust sapwood were 12.10 and 7.92% respectively, and from lemonwood 15.93 and 9.50%.[36] Such a difference cannot be regarded as evidence of efficiency in separation, however, because another explanation is possible. As mentioned earlier, most workers in fractionating hemicellulose extracts have consistently ignored the contribution made from the cellulose. It has been established by extraction from isolated cellulose, free of polyuronide hemicelluloses, that the cellulosans are simple polysaccharides containing one constituent group only. The most widespread cellulosan is undoubtedly xylan. Though virtually homogeneous as far as constituent groups are concerned, the cellulosans are unlikely to be uniform in respect to chain length. If put through the fractionation system applied to hemicellulose extracts, xylan, at least, appears predominantly in the less-soluble fractions, but by no means exclusively so. There is, therefore, the real possibility that differences in uronic content between the less-soluble and more-soluble fractions precipitated from combined alkaline extracts may be due in part to decreasing amounts of xylan or other cellulosan precipitated along with the polyuronide hemicelluloses as the alcohol concentration is raised. This explanation is supported by an examination of the analyses obtained on the hemicellulose extracted from white pine[41] the cellulosan fraction of which would be expected to contain both mannan and xylan. Mannan appeared in all fractions, and indeed the authors recognized the presence of "a mannan free of a uronic acid." They also presumed mannose units to be present in the truly polyuronide fraction, but the published evidence does not make clear how it was established that this was the case, or that simple mixture was not involved. Similarly, the extraction of maple holocellulose with alkaline solutions of increasing concentrations yielded preparations having respectively 28.9, 12.2, and 6.5% urone with increasing pentosan contents, no doubt in part due to concurrent cellulosan extraction.[45]

From a wide range of plant materials, mostly lignified, preparations have been obtained that appeared to consist of xylose and monomethoxyglucuronic acid in proportions varying from 6 to 12 or more xylose units per hexuronic group. The methoxyl group is extremely stable and resists treatment with either acid or alkali. Hydrolysis of such preparations may yield a stable aldobiuronic acid consisting of one xylose group linked to methoxyhexuronic acid, which is not further resolved by long boiling with acid. Acids containing two pentose units linked to one methoxyhexuronic acid group have also been obtained. These have contained only one reducing group and therefore are probably the terminal units of a straight chain.

The hemicelluloses from corn cobs have perhaps been most studied, and in this case the main fraction is predominantly a xylan. Extraction of the holocellulose by dilute potassium hydroxide removes a fraction containing substantially more uronic groups.[47] The main xylan fraction, which goes into solution only when a higher concentration of alkali is used, gives on hydrolysis with dilute acid a high yield of D-xylose. Crystalline oligosaccharides have also been prepared and shown to contain the β-1,4-glycosidic linkage.[48] Relatively short-chain crystalline xylans have been prepared by autoclaving an aqueous paste of the purified hemicellulose fraction removed by 5% NaOH from barley straw and paper birch holocellulose.[49] By osmotic pressure measurements these xylans were shown to have a degree of polymerization (D.P.) of 39.2 and 35 respectively.

Early methylation studies on esparto xylan resulted in the unexpected conclusion that the chains of D-xylopyranose units were probably terminated by one L-arabofuranose unit.[50] This conclusion was revised when it became apparent that the arabinose arose from an araban which could progressively be removed from the xylan by careful purification. Hydrolysis of purified xylan preparations methylated with alkaline methyl sulfate to 38.6% methoxyl content yielded a mixture of the glycosides of 2,3,4-trimethyl-, 2,3-dimethyl-, and 2-monomethyl-D-xylopyranose. The quantitative relationship between these methanolysis products indicates a molecule with a simple branched structure, the linkage at the point of branching being of the C_1-C_3 type. Various types of information point to a chain length of about 75 xylose units. No uronic groups are present.[51]

A somewhat more complicated structure is present in pear cell-wall xylan, which consists essentially of a Y, the arms of which are composed of xylose units linked through the 1,4-positions but with a D-glucuronic unit[52] attached as a branch to the penultimate xylose unit of one of the arms.

The hemicellulose from *Phormium tenax* (New Zealand flax) has similarly been subjected to exhaustive methylation and hydrolysis.[53,54] In this product uronic units are characteristically present, so that on methanolysis there is obtained a mixture of methylxylosides, and a methylated aldotrionic acid. Although about 11% of the product was 2,3,4-trimethyl methylxyloside, the main portion consisted of 2,3-dimethylmethylxyloside. This points to a chain of about ten xylopyranose residues linked through the 1,4-positions terminated at the reducing end by an aldotrionate containing a hexuronic group. Oxidative and hydrolytic studies on the methylated aldotrionic acid indicate that it is composed of two D-xylose residues, one linked through positions 1 and 4 and the other through positions 1, 2, and 4, to which is attached terminally D-glucuronic acid. The molecule as a whole therefore has a simple branched structure, in which the aldotrionic acid constitutes a side chain arising perhaps near the center of a normal 1,4-xylopyranose chain.

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[47] R. L. Whistler, D. R. Bowman, and J. Bachrach, *Arch. Biochem.*, **19**, 25 (1948).

[48] R. L. Whistler and C. C. Tu, *J. Am. Chem. Soc.*, **74**, 3609, 4334 (1952).

[49] A. P. Yundt, *Tappi*, **34**, 89 (1951).

[50] R. A. S. Bywater, W. N. Haworth, E. L. Hirst, and S. Peat, *J. Chem. Soc.*, **1937**, 1983.

[51] S. K. Chandra, E. L. Hirst, J. K. N. Jones, and E. G. V. Percival, *J. Chem. Soc* **1950**, 1289.

[52] S. K. Chandra, E. L. Hirst, and E. G. V. Percival, *J. Chem. Soc.*, **1951**, 1240.

From numerous sources preparations have been obtained, which, like the *Phormium tenax* hemicellulose, appeared to consist predominantly of xylose and glucuronic acid units, the latter often being methylated. No good purpose would be served by citing these results individually since few have been examined in as detailed a manner as those described in the last few paragraphs. It may well be that many of these preparations consisted of mixtures of polysaccharides containing uronic groups with uronic-free polysaccharides, as typified by the xylan obtained from esparto. Corn cob preparations certainly conform to this description, with xylan predominating. In such cases at least a part of the xylan is extracted from the cellulose. The true uronic content of the polyuronide fraction is, therefore, likely to be considerably higher or at least the proportion of xylan to uronic groups is likely to be lower. That this is highly probable may be seen from the work of Mitchell and Ritter.[21] From maple holocellulose they obtained hemicellulose fractions that, because of the mild means of extraction used, would be unlikely to contain any appreciable amount of xylan from the cellulose. Preparations removed by hot water and dilute sodium carbonate contained approximately three xylose groups per uronic unit. When more drastic extracting agents were used (cold 4% and hot 10% NaOH), the proportions increased to roughly 8 and 10 xylose groups per uronic unit, respectively. The fractions extracted by water and carbonate represented, however, only about 25% of the material extracted. Another feature of this work on maple holocellulose was the observation that the hemicelluloses may have acetyl groups normally linked to them.

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[53] R. J. McIlroy, *J. Chem. Soc.*, **1945**, 796.

[54] R. J. McIlroy, *J. Chem. Soc.*, **1949**, 121.

Approximately 9% acetyl was found in the water-soluble fraction, and this, of course, would ordinarily be missed if alkaline extractions were employed.

Although the majority of the hemicelluloses studied recently have been of the xylan–glucuronide type, preparations from nonlignified sources have been found to contain arabinose, galactose, and galacturonic acid. Buston has suggested that this is characteristically the case, but insufficient studies have been made to permit of such a generalization. In preparations from certain grasses, leaves, and pods, galactose has been the preponderant constituent.[11]

No generalization about the structures of polyuronide hemicelluloses is yet possible because relatively few preparations have been subjected to detailed study by the newer procedures. Most preparations are of relatively low uronic content. Their properties are consistent with a chain structure uniformly linked and terminating in a uronic group. Good evidence exists for the belief that some branching may occur but in some cases, at least, the branching is relatively simple, and not complex enough to prevent the formation of films on acetylation.[55] Molecular-size determinations by various methods yield results which are somewhat divergent, but all indicate much smaller numbers of sugar units than are found in cellulose or starch. Molecular weight figures of the order of 4000 to 11,000 have been obtained on preparations from various sources.[51,56,57] Undoubtedly considerable variation exists in molecular sizes, and it is possible that the alkaline extractants used may at elevated temperatures result in some degradation or chain shortening.

6. Pectin

The pectic substances are found in all young plant tissues and are characteristic constituents of fruits and fleshy roots. In tissues that become lignified and in which secondary thickening of the cell wall takes place, the pectic content rapidly diminishes, though some calcium or calcium-magnesium pectate may persist to maturity in the middle lamella and can be isolated from mature wood.[58] In contrast to the relatively low uronic content of the hemicelluloses, the pectic substances have long been recognized as being predominantly polyuronide in nature, and are now considered to consist almost exclusively of galacturonic units. Most of the carboxyl groups of the pectin molecule *in situ* are esterified. The water-insoluble form, protopectin, may be removed from the cell wall of unlignified tissues by extraction with warm dilute acids, such as 0.5% oxalic acid, or even 0.5% ammonium oxalate. It is undoubtedly the precursor of the water-soluble modification, known as pectin or pectinic acid, that occurs particularly in fruits and is formed enzymatically in the process of ripening and senescence. Protopectin was believed by some to be a pectin-cellulose complex (pectocellulose) but the evidence in favor of such a view is far from strong and the theory is hardly compatible with present-day ideas as to the molecular structure of either cellulose or pectin. More probably the water insolubility of protopectin arises from the great length of the polygalacturonide chains, which if shortened or broken into shorter sections yield galacturonides which then are water-soluble. The insolubility of the pectic substances of the cottonseed hair[59] is believed to be due, however, to the presence of bound calcium and other polyvalent metal ions.

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[55] C. L. Smart and R. L. Whistler, *J. Polymer Sci.*, **4**, 87 (1949).

[56] M. A. Millett and A. J. Stamm, *J. Phys. & Colloid Chem.*, **51**, 134 (1937).

[57] E. Bennett, *J. Agr. Research*, **75**, 43 (1947).

[58] W. W. Pigman, E. Anderson, and R. L. Leaf, Jr., *J. Am. Chem. Soc.*, **70**, 432 (1948).

In the case of pectin preparations, as with other cell-wall polysaccharides, good criteria of purity are lacking. Extraction may be carried out by comparatively mild methods, but the products obtained vary in galacturonide content, in viscosity, and in the ability to form jellies with sugar and acid. The crude preparations obtained by many workers and by various methods usually contain about 70 to 80% galacturonide, the remainder of the preparation being accounted for by arabinose and galactose units. By treatment with dilute alkali or dilute acid, the galacturonide content of the preparations can be caused to rise, and indeed a substantially pure polygalacturonide can be obtained by such means. Such products, however, often have greatly reduced viscosity and jellying power which are indicative of molecular disaggregation or reduced molecular size. Although for some time the pectin molecule was believed to consist of a galacturonide to which were linked arabinose and galactose, the present view is that the pectin molecule is essentially a long straight-chain polygalacturonide and that the arabinose and galactose arise from arabans and galactans present with the pectin but not a part of it. The sum of the carboxyl groups which are uncombined, salt-linked, or esterified is equal to the total number of galacturonic groups in the pectin.[60] Exhaustive methylation followed by methanolysis yields almost exclusively the methyl ester of 2,3-dimethyl methyl-D-galacturonoside.[61]

A long-chain molecular structure for pectin was deduced from osmotic pressure, viscosity,[62] and x-ray studies[63] and values of from 30,000 to 100,000 were obtained for the molecular weight.[64–66] Short-chain fragments of 8 to 13 units have been obtained by treatment of pectic acid with dry methanol and hydrochloric acid[67] or by complete methylation.

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[59] R. L. Whistler, A. R. Martin, and M. Harris, *J. Research Natl. Bur. Standards*, **24**, 555 (1940).

[60] M. Hamer, *Makromol. Chem.*, **4**, 184 (1949).

[61] G. H. Beavan and J. K. N. Jones, *J. Chem. Soc.*, **1947**, 1218.

The methylated product obtained from citrus and apple pectin behaves as if essentially a homogeneous molecule of molecular weight about 6000 corresponding to the methyl ester of a polygalacturonide consisting of 32 galacturonic acid units.[68] The view has been expressed that structural units of this type are repeated in the protopectin macromolecule perhaps being linked together by a linkage less strong than the normal 1,4-glycosidic bond.

The physical chemistry of pectin is particularly difficult because the pectin molecule, the dimensions of which apparently can vary enormously, has also the peculiarity of having a variable equivalent weight depending on the degree of esterification with methyl groups. The property of jellying is more closely related to chain length than to methoxyl content. Beet pectin, however, though possessing a molecular weight of 20,000–25,000 will not form rigid jellies. The high viscosity of pectin in solution is regarded as additional evidence of large molecular dimensions.

The observation that the pectin substances decrease in proportion to other cell-wall constituents as plant tissues mature has led to the suggestion that pectin may undergo transformation to hemicelluloses or lignin. Very little evidence in support of such theories has been adduced, and indeed in the only attempt that has been made to test them experimentally, the pectic substances have been found to possess a high degree of stability.

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[62] H. S. Owens, H. Lotzkar, T. H. Schultz, and W. D. Maclay, *J. Am. Chem. Soc.*, **68**, 1628 (1946).

[63] K. J. Palmer, *J. Applied Phys.*, **17**, 405 (1946).

[64] F. A. Henglein and G. Schneider, *Ber.*, **69B**, 309 (1936).

[65] G. Schneider and M. Ziervogel, *Ber.*, **69B**, 2530 (1936).

[66] G. Schneider and U. Fritschi, *Ber.*, **69B**, 2537 (1936).

[67] S. Morrell, L. Baur, and K. P. Link, *J. Biol. Chem.*, **105**, 1 (1934).

[68] E. F. Jansen, L. R. MacDonnell, and W. H. Ward, *Arch. Biochem.*, **21**, 149 (1949).

C. LIGNIN AND OTHER NONCARBOHYDRATES

F. E. BRAUNS

1. Occurrence, State of Linkage, Color Reactions, Determination, and Physical Properties of Lignin

Cellulose occurs in nature in a relatively pure state in seed hairs; in wood and other lignified materials it is associated with hemicelluloses, pentosans, polyuronides, and noncarbohydrate components consisting chiefly of lignin, together with small amounts of tannins, resins, fats, and a few other minor constituents.

Although lignin, like cellulose, has given rise to a special field in organic chemistry,[1] the literature of which has grown tremendously during the past twenty-five years, the close association of lignin with cellulose warrants discussion in a treatise on the latter. Unlike cellulose, lignin has never been found alone in nature but is always associated with carbohydrates. Because the cellulose chemist is interested primarily in the separation of cellulose from noncellulosic components, the chemistry of lignin will be discussed with special reference to the occurrence of lignin in the plant, its separation from cellulose for the production of wood and straw cellulose, and the purification of unbleached wood pulps—that is, the chemical reactions used in the removal of the residual lignin.

(a) OCCURRENCE

In wood (see Section A of this Chapter V), lignin is located chiefly in the middle lamella, from which it penetrates in gradually diminishing amounts into the primary and secondary layers of the cell wall. In straw and other annual plants, lignin seems to be mainly on the surface of the fiber and in a less highly condensed state, since it can be removed much more readily than from wood.[2]

Whereas the polysaccharides, such as cellulose, hemicellulose, pentosans, and polyuronic acids, are fairly readily hydrolyzed to simple water-soluble sugars by the action of mineral acids, lignin seems to be stable under such treatment. This difference is utilized for the separation of lignin from carbohydrates by saccharification of the latter. Lignin, therefore, may be defined as the part of wood and straw that remains as an insoluble product when such lignified materials, after removal of the tannins, resins, and other extractives, are treated with strong mineral acids. Lignin also differs from cellulose in having a high content of methoxyl groups which are attached to aromatic rings of the lignin molecule.[3] The early belief[4] that all the methoxyl groups in wood are attached to lignin has been found to be incorrect,[5] since some of them seem to be combined with uronic acids. Recently, however, it has again been claimed[6] that all the methoxyl groups in wood pertain to the lignin and that the lignin content of wood is actually higher than that hitherto assumed. Although it has been definitely shown[7,8] that the lignin in coniferous woods differs structurally from that in deciduous woods, the structural relationship of lignin in annual plants to that in wood has not yet been definitely established. Moreover, the origin of lignin is still unknown, although there has been much speculation as to the possibility of its being derived from carbohydrates.[9,10]

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[1] F. E. Brauns, *The Chemistry of Lignin*, Academic Press, New York, 1952.

[2] E. Beckmann, O. Liesche, and F. Lehmann, *Z. angew. Chem.*, **34**, 285 (1921)· *Biochem. Z.*, **139**, 491 (1923).

(b) NATURE OF THE ASSOCIATION OF LIGNIN IN WOOD[11]

The study of lignin is rendered extremely difficult because of its chemical and physical properties. The claim[12,13] that lignin does not exist in the plant but is a secondary reaction product formed by the action of the reagents used for its isolation on reactive, partly methylated carbohydrates can no longer be maintained because its existence as an aromatic compound has been definitely proved.[14,15]

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[3] K. Freudenberg, W. Belz, and C. Niemann, *Ber.*, **62B**, 1554 (1929).

[4] R. Benedikt and M. Bamberger, *Monatsh.*, **11**, 269 (1890).

[5] G. J. Ritter and J. H. Barbour, *Ind. Eng. Chem., Anal. Ed.*, **7**, 238 (1935).

[6] A. von Wacek and D. Schroth, *Das Papier*, **4**, 410 (1950); *Monatsh.*, **81**, 1151 (1950); *Holz Roh- u. Werkstoff*, **9**, 7 (1951).

[7] K. Freudenberg, *Tannin, Cellulose, Lignin*, J. Springer, Berlin, 1933.

[8] R. H. J. Creighton, R. D. Gibbs, and H. Hibbert, *J. Am. Chem. Soc.*, **66**, 32 (1944).

[9] P. Klason, *Ber.*, **56B**, 300 (1925).

[10] K. Freudenberg, *Ann. Rev. Biochem.*, **8**, 107 (1939); *Fortschr. Chem. org. Naturstoffe*, **2**, 1 (1939).

[11] A part of this section has been taken from C. B. Purves' earlier contribution, Chapter II, Section F, of the first edition of this volume (Vol. V, High Polymer series).

[12] R. S. Hilpert and H. Hellwage, *Ber.*, **68B**, 380 (1935); R. S. Hilpert, *Cellulosechemie*, **17**, 25 (1936).

[13] F. Schütz and P. Sarten, *Cellulosechemie*, **21**, 35 (1943); **22**, 1, 114 (1944); F. Schütz, P. Sarten, and H. Meyer, *Holzforschung*, **1**, 2 (1947).

The nature of the association of lignin with other constituents in lignified material is of particular interest to the cellulose chemist because the isolation of cellulose is closely related to the presence or absence of a chemical linkage. This is still an open question, although recently the belief that at least the major part of the lignin is combined with carbohydrates has gained more and more ground.[16–18] A small percentage of lignin is present in coniferous and deciduous woods in a free state; this can be extracted with suitable indifferent solvents, such as dioxane or alcohol, in the absence of a catalyst.[19] This "isolated native lignin" is undoubtedly a chemically unchanged protolignin, a lignin as it occurs in the plant. An additional small amount of the same lignin can be isolated by a similar extraction from a wood which, after the removal of "extractable native lignin," is exposed to the action of certain fungi of the brown rot type.[20] The claim[20] that this "enzymatically liberated native lignin" is present in wood in a free uncombined state is valid, however, only after it has been proved that the enzymes of these fungi do not split a possible lignin–carbohydrate linkage. The fact remains that the major part of the lignin in lignified materials can be isolated only by the use of drastic reactions which undoubtedly modify its nature.

That only a small percentage of lignin can be isolated in an unchanged condition does not necessarily imply that the remainder is chemically combined with other wood components. It may be absorbed on other wood constituents or it may be present in a very high molecular state which prevents its solution in indifferent lignin solvents. The claim[21] that lignin can be dissolved from aspen almost quantitatively by aqueous butanol at 160°C. was interpreted to mean that the lignin in aspen is present in a free state. From pine about 80% was removed under these conditions and was believed to be free, whereas the residual 20% was considered to be chemically com-

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[14] P. Lange, *Svensk Papperstidn.*, **47**, 263 (1944); **48**, 241 (1945).

[15] F. E. Brauns, Paper presented at the XII International Congress, New York City, Sept. 11, 1951.

[16] B. Holmberg and S. Runius, *Svensk Kem. Tid.*, **37**, 189 (1925).

[17] F. E. Brauns, *Paper Trade J.*, **111**, 33 (Oct. 3, 1940).

[18] Ø. Bryde and B. Rånby, *Svensk Papperstidn.*, **50**, No. 11B, 34 (1947).

[19] F. E. Brauns, *J. Am. Chem. Soc.*, **61**, 2120 (1939); *J. Org. Chem.*, **10**, 211 (1945).

[20] W. J. Schubert and F. F. Nord, *J. Am. Chem. Soc.*, **72**, 977, 3835 (1950); *Holzforschung*, **5**, 1 (1951); S. F. Kudzin and F. F. Nord, *J. Am. Chem. Soc.*, **73**, 690 (1951).

[21] A. J. Bailey, *Paper Trade J.*, **110**, 29 (Jan. 4, 1940); see, however, H. Y. Charbonnier, *Paper Trade J.*, **114**, 31 (Mar. 12, 1942).

bined because it could be dissolved only after the addition of sodium hydroxide. When wood, particularly hardwood, is heated with water at superatmospheric pressure, acids are formed[22]; hence the above conclusion is unwarranted. Harris and coworkers[23] interpreted their results differently. They subjected maplewood to a methylation with dimethyl sulfate and sodium hydroxide under conditions adequate to methylate isolated lignin and obtained from the methylated wood a lignin with an unchanged methoxyl content. When the wood was first subjected to a mild hydrolysis with 1% H_2SO_4, the methoxyl content of the lignin increased to 28%, from which they concluded that the hydroxyl groups of the lignin in the untreated wood are masked by a combination with other wood components. Several other investigators,[24–26] however, have shown that the lignin in sprucewood can be methylated with dimethyl sulfate to the extent of about 26% without prehydrolysis, which is still about 4–5% below the methoxyl content of fully methylated isolated native spruce lignin. Since fully methylated hydrochloric acid spruce or isolated native spruce lignin loses methoxyl groups on treatment with reagents of an acid nature,[27] the lignin of a methylated sprucewood may likewise lose methoxyl groups during its isolation, and the lignin in such a wood may actually have been methylated to a higher degree. Recent work with colloidal wood solutions[15] also seems to support the concept that lignin is chemically combined with other wood constituents.

The assumption that a linkage exists between lignin and another component gives rise to the question of the identity of this component. Because a definite lignin–carbohydrate complex from which the carbohydrate component can be isolated and identified has not yet been obtained, it is impossible to decide with which part of the holocellulose lignin may be combined. According to Bailey,[28] the middle lamella of sprucewood consists of about 70% lignin and 30% pentosans, in which case the lignin can be attached only to pentosans. From the action on basswood (linden) of the enzymes isolated from the digestive juice of the vineyard snail, *Helix pomatia*, Ploetz[29] obtained preparations which contained in the unhydrolyzed residue a weight ratio of carbohydrate to lignin of 3:1 and 1:1

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[22] S. I. Aronovsky and R. A. Gortner, *Ind. Eng. Chem.*, **28**, 1270 (1936).

[23] E. E. Harris, E. C. Sherrard, and R. L. Mitchell, *J. Am. Chem. Soc.*, **56**, 889 (1934).

[24] H. Urban, *Cellulosechemie*, **7**, 73 (1926).

[25] F. E. Brauns and H. Hibbert, *Can. J. Research*, **13B**, 78 (1935).

[26] F. E. Brauns and D. S. Brown, *Ind. Eng. Chem.*, **30**, 779 (1938).

[27] F. E. Brauns, *J. Am. Chem. Soc.*, **68**, 1721 (1946).

[28] A. J. Bailey, *Ind. Eng. Chem., Anal. Ed.*, **8**, 389 (1936).

[29] T. Ploetz, *Ber.*, **72B**, 1885 (1939): **73B**, 57, 61, 74, 790 (1940); K. Freudenberg and T. Ploetz, *Ber.*, **73B**, 754 (1940).

and no pentosans. A somewhat similar result was obtained by Smith and Purves[30] who found a 1:1 lignin-to-carbohydrate ratio in a very finely ground fraction of cottonseed hull containing up to 10% of the original lignin. The carbohydrates consisted largely of uronic acid and contained little or no pentosans. The fact that sodium sulfite does not remove much hemicellulose from wood unless the lignin is first rendered soluble by chlorination led Norman and Shrikhande[31] to conclude that a chemical linkage exists between these two wood components. When wood, regenerated from its solution in cuprammonium hydroxide, is extracted with alcohol or dioxane, in which isolated native lignin is soluble, no lignin is removed.[15] If the lignin were present as a separate wood constituent, it would be logical to expect it to go into solution.

The strong indications of the existence of a chemical lignin–carbohydrate bond lead to the question of its nature. In lignin the reactive groups which may participate in such a linkage are phenolic and aliphatic hydroxyl groups and an enolizable carbonyl group; in the carbohydrates there are primary and secondary hydroxyl groups, an aldehydic carbonyl group, and the carboxyl groups of the uronic acids. Since ether linkages are too stable to be split by the methods used for the isolation of lignin, these are unlikely to be present. Acetal or hemiacetal linkages between the carbonyl group of the lignin and the hydroxyl groups of the polysaccharides have been considered.[9,16,32] Because the phenolic group in lignin is still free in wood,[26] it seems improbable that this group participates in a lignin–carbohydrate linkage. An ester linkage between the uronic acid and lignin would be much too unstable.

(c) COLOR REACTIONS

Lignin can be detected by certain color reactions, particularly with aromatic amines and phenols and some heterocyclic compounds of the furan and pyrrole type.[33–35] Of these reactions, the one with phloroglucinol and hydrochloric acid is the most commonly used. It is known as the Wiesner color reaction[36,37] and gives a bright purple color. None of these color reactions, however, is specific for lignin, since some aldehydes, such as coniferyl aldehyde, give similar colorations. There is no longer any doubt that with woods the color reactions are given by the lignin.[17,38] Isolated native spruce lignin gives a deep purple color with Wiesner reagent, but, when methylated with diazomethane, neither sprucewood nor isolated native spruce lignin gives the color reaction[17] which is attributed to a coniferyl aldehyde group in the lignin molecule.[39] The Mäule reaction,[40] in which lignin material is treated successively with dilute potassium permanganate solution, dilute hydrochloric acid, and ammonium hydroxide, and which gives a bright purple color with deciduous woods, may be used for the differentiation between these and coniferous woods, since the latter give only an indistinct brownish color.[8] With supersaturated hydrochloric acid, isolated native spruce lignin gives the same bright emerald color as given by sprucewood itself.[19,41]

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[30] M. A. Smith and C. B. Purves, *Ind. Eng. Chem., Anal. Ed.*, **13**, 157 (1941).

[31] A. G. Norman and J. G. Shrikhande, *Biochem. J.*, **29**, 2258 (1936).

[32] F. E. Brauns, *The Chemistry of Lignin*, Academic Press, New York, 1952, p. 684.

[33] M. Phillips, *Chem. Revs.*, **14**, 103 (1934).

[34] F. E. Brauns, *The Chemistry of Lignin*, pp. 26–48.

[35] G. A. Moerke, *J. Org. Chem.*, **10**, 42 (1945).

[36] J. Wiesner, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse*, **77**, 60 (1878).

[37] J. C. Pew, *J. Am. Chem. Soc.*, **73**, 1678 (1951).

(d) QUANTITATIVE DETERMINATION

Numerous methods have been proposed for the quantitative determination of lignin, the most common being based upon the use of 72% H_2SO_4 as originally suggested by Klason[42] and as developed by the Forest Products Laboratory, Madison, Wisconsin. This method is suitable for coniferous woods and unbleached wood pulps but not for deciduous woods.[17,29] For the latter, the concentration of sulfuric acid which gives the highest lignin yield with the highest methoxyl content must be determined for each wood species.[29] If a lignin from a sulfite or kraft pulp is to be analyzed for sulfur, 42% HCl should be used for the lignin determination.[43] Because the lignin in chemical pulps is changed[43,44] by the effect of the pulping reagent, a part of the lignin may have been rendered soluble, particularly in sulfite pulps, and the results may be misleading. Whatever method is applied, it is important that a finely ground plant material be used and that before analysis it be extracted by an alcohol–benzene mixture (1:2) to remove extractives which otherwise would interfere in the determination. In some instances, particularly with woods high in tannin content, an extraction with water or even with dilute sodium hydroxide may be advisable.

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[38] K. Wiechert, *Papier-Fabr.*, **37**, Tech.-wiss. Tl., **17**, 30 (1939).

[39] E. Adler, K. J. Björkqvist, and S. Häggroth, *Acta Chem. Scand.*, **2**, 93 (1948); E. Adler and L. Ellmer, *Acta Chem. Scand.*, **2**, 859 (1948).

[40] C. Mäule, *Beitr. Z. wiss. Botan.*, **4**, 166 (1900).

[41] F. A. Abadie, *Norsk Skogsind.*, **3**, 290 (1949).

[42] P. Klason, *Beiträge zur Kenntnis der chemischen Zusammensetzung des Fichtenholzes*, Borntraeger, Berlin, 1911.

[43] L. L. Larson, *Tech. Assoc. Papers*, Ser. **24**, 243 (1941).

[44] C. E. Ahlm, *Paper Trade J.*, **113**, 115 (Sept. 25, 1951).

Such a treatment must be carried out with exclusion of air and may be accompanied by a small loss of lignin.[45–48]

(e) PHYSICAL PROPERTIES

Isolated native spruce lignin is a light cream-colored powder, soluble with a reddish-brown color in dioxane and other organic solvents,[19] whereas lignins obtained by the removal of the carbohydrates still show the mor-

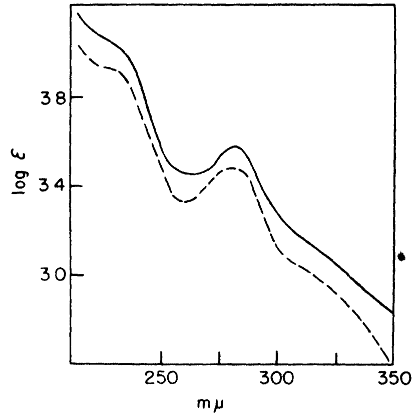

Fig. 11. Ultraviolet absorption spectra of native spruce lignin (—) and of lignosulfonic acid (- - - -). The ordinate is the logarithm of the extinction coefficient; the abscissa is wavelength in millimicrons.

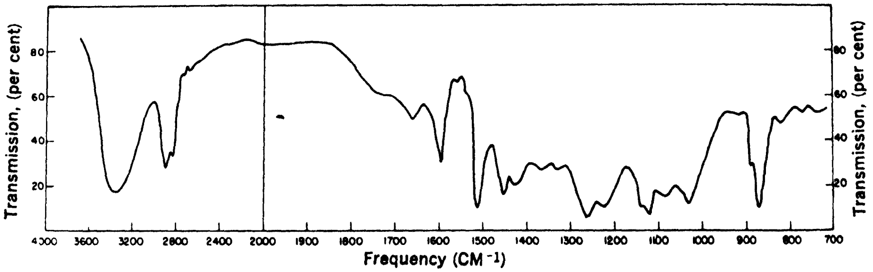

Fig. 12. Infrared absorption spectrum of native black spruce lignin (film from dioxane and ethyl alcohol).

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[45] A. Friedrich and J. Diwald, *Monatsh.*, **46**, 31 (1925).

[46] K. Freudenberg, M. Harder, and L. Markert, *Ber.*, **61B**, 1762 (1928).

[47] K. Freudenberg, H. Zocher, and W. Dürr, *Ber.*, **62B**, 1814 (1929).

[48] H. Hibbert and E. G. King, *Can. J. Research*, **14B**, 12 (1936).

phological structure of the plant fiber,[47] are light to dark brown in color (varying with the mode of isolation), and are insoluble in all solvents. The organosolv lignins are soluble in various organic solvents and in cold dilute alkali. Lignin is optically inactive[49] and has a refractive index of 1.61.[3,47,50] Its x-ray pattern shows lignin to be amorphous.[51–55] From spreading experiments with sodium lignoazobenzenesulfonate a layer thickness of 15–20 A. has been found, indicating a three-dimensional structure.[3] The ultraviolet absorption spectrum of lignin indicates its aromatic structure[56–61] (see Fig. 11). Its infrared absorption curve shows the presence of aromatic rings, saturated aliphatic groups, hydroxyl groups, and a weak but definite band at 1663 cm.$^{-1}$, commonly associated with carbonyl groups or aliphatic double bonds. Since this band disappears when the lignin is treated with methyl alcohol and hydrochloric acid, it would seem to originate from a carbonyl group (Fig. 12).[62] Acid lignins have a high molecular weight[63,64]; moreover, isolated native spruce lignin has a molecular weight of 860.[65] Lignosulfonic acids vary considerably in molecular weight, depending upon the conditions under which they are prepared; they show an ultraviolet absorption curve very similar to that of native lignin (see Fig. 11), indicating that no deep-seated change occurs in the lignin structure during the sulfonation.[60] There is little doubt that lignin is built up, according to a definite pattern, from building stones belonging to a group of biochemically related types. For the lignin building unit, a molecular weight of about 840 has been calculated, corresponding to five phenylpropane building stones, each with a molecular weight of about 170.[66,67]

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[49] K. Freudenberg and F. Sohns, *Ber.*, **66B**, 262 (1933).

[50] K. Freudenberg, F. Sohns, W. Dürr, and C. Niemann, *Cellulosechemie*, **12**, 263 (1931).

[51] E. Wedekind and J R. Katz, *Ber.*, **62B**, 1172 (1929).

[52] E. E. Harris, E. A. Parker, E. C. Sherrard, and G. L. Clark, *Biodynamica*, No. **31**, 12 pp. (1937–1938).

[53] P. Nilakantan, *J. Indian Inst. Sci.*, **A5**, 166 (1937).

[54] R. Jodl, *Brennstoff-Chem.*, **23**, 163 (1942).

[55] H. Zahn and W. Lautsch, *Kolloid-Z.*, **110**, 82 (1948).

[56] R. O. Herzog and A. Hillmer, *Ber.*, **60B**, 354, 1600 (1927); **64B**, 1288 (1931).

[57] E. Hägglund and E. W. Klingstedt, *Svensk Kem. Tid.*, **41**, 185 (1929); *Z. physik. Chem.*, **A152**, 295 (1931).

[58] R. E. Glading, *Paper Trade J.*, **111**, 32 (Dec. 5, 1940).

[59] R. F. Patterson and H. Hibbert, *J. Am. Chem. Soc.*, **65**, 1862, 1869 (1943).

[60] G. Aulin-Erdtman, *Svensk Papperstidn.*, **47**, 91 (1944).

[61] A. W. Sohn, *Das Papier*, **4**, 379 (1950).

[62] E. J. Jones, *J. Am. Chem. Soc.*, **70**, 1984 (1948); *Tappi*, **32**, 411 (1949).

[63] D. L. Loughborough and A. J. Stamm, *J. Phys. Chem.*, **40**, 1113 (1936).

[64] N. J. Gralén, *J. Colloid Sci.*, **1**, 453 (1946).

[65] E. J. Jones, private communication.

2. Methods of Isolation of Lignin

(a) LABORATORY PROCEDURES

With the exception of a small fraction (about 8%), lignin cannot be isolated in an unchanged state. The methods used for its isolation for scientific research may be divided into two groups: those in which the carbohydrates are removed by hydrolysis, by a solvent, or by oxidative degradation, leaving the lignin as an insoluble residue; and those in which the lignin is dissolved by suitable reagents in the presence of an acid catalyst, whereby most of the holocellulose is obtained as a more or less lignin-free residue, depending upon the reagents used.

For the hydrolysis of the carbohydrates in the first type of isolation, 64–72% sulfuric acid,[68] 42% hydrochloric acid,[69] hydrofluoric acid,[70] or a mixture of acids may be used.[71,72] These methods have often been modified. The carbohydrates may also be extracted from wood with cuprammonium hydroxide, after a mild prehydrolysis with boiling 1% H_2SO_4 or 7% oxalic acid.[46] This prehydrolysis seems to be necessary, as otherwise only a small amount of the polysaccharides is dissolved, which supports the concept that lignin is chemically combined with carbohydrates. By repeated alternate hydrolysis and extraction, so-called cuoxam lignin is obtained as a light brown powder. An interesting method for the isolation of lignin from wood utilizes the oxidation of the carbohydrates with periodic acid and the hydrolysis of the polysaccharide aldehydes with hot water, thus rendering the carbohydrate portion water soluble.[73] The lignins so obtained resemble other insoluble lignins in many respects, but whether they are unchanged by the periodic acid remains to be proved.

In the second type of isolation, an organic solvent (generally in the presence of a small amount of hydrochloric acid or other acid catalyst), or an

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[66] F. E. Brauns and H. Hibbert, *Can. J. Research*, **13B**, 28 (1935).

[67] P. B. Sarkar, *J. Indian Chem. Soc*, **11**, 691 (1934).

[68] P. Klason, *Cellulosechemie*, **4**, 81 (1923); **12**, 36 (1931).

[69] R. Willstätter and L. Kalb, *Ber.*, **55B**, 2637 (1922); L. Kalb and T. Lieser, *Ber.*, **61B**, 1007 (1928).

[70] K. Wiechert, *Cellulosechemie*, **18**, 57 (1940).

[71] H. Urban, *Cellulosechemie*, **7**, 73 (1926).

[72] K. Freudenberg and M. Harder, *Ber.*, **60B**, 581 (1927).

[73] P. F. Ritchie and C. B. Purves, *Pulp & Paper Mag. Can.*, **48**, 74 (1947); W. Wald, P. F. Ritchie, and C. B. Purves, *J. Am. Chem. Soc.*, **69**, 1371 (1947).

inorganic reagent, or a combination of both is used. In all extractions of lignin by means of organic solvents in the presence of a catalyst, the solvent condenses with the lignin and gives a lignin derivative. On refluxing pre-extracted sprucewood 6 to 10 hrs. with ethanol containing 5% hydrogen chloride, concentrating the solution, and pouring it into water, Klason[74] obtained an ethanol spruce lignin which differed from the original lignin through the presence of ethoxyl groups resulting from a condensation of the lignin with the ethanol. Similar reactions have been applied to various mono- and poly-hydroxy alcohols such as methanol,[66] ethanol,[16,45,75–78] butanol,[79] isobutanol,[80] amyl alcohol,[80] ethylene glycol,[81–84] glycol monomethyl ether,[84–86] benzyl alcohol,[87] cyclohexanol,[87] chlorohydrin,[82] glycerol α-monochlorohydrin,[86] and ethanolamine.[88] The newly attached alkoxy groups are split off again with mineral acids but not without a change in the lignin. Isolated native spruce lignin reacts with methanol in the presence of hydrogen chloride with the formation of a methanol lignin having two new methoxyl groups.[19] Carefully purified dioxane in the presence of 0.5% hydrogen chloride does not dissolve lignin.[89–94]

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[74] P. Klason, *Tek. Tid.*, **23**, Uppl. C., 55 (1893).

[75] J. Grüss, *Ber. deut. botan. Ges.*, **38**, 361 (1920); **41**, 48 (1923).

[76] A. Friedrich and B. Brüda, *Monatsh.*, **46**, 600 (1925).

[77] H. Hibbert and coworkers, *J. Am. Chem. Soc.*, **60**, 2815 (1938); **61**, 516, 868, 2196 (1939); **62**, 2803 (1940); **66**, 39 (1944).

[78] B. Holmberg, *Svensk Papperstidn.*, **50**, 11B, 111 (1947).

[79] H. Y. Charbonnier, *Paper Trade J.*, **114**, 31 (Mar. 12, 1942).

[80] E. Hägglund and H. Urban, *Cellulosechemie*, **8**, 69 (1927); **9**, 49 (1928).

[81] H. Gabriel, Dissertation, Leipzig, 1928; B. Rassow and H. Gabriel, *Cellulosechemie*, **12**, 227, 290, 318 (1931).

[82] H. Hibbert and coworkers, *Can. J. Research*, **2B**, 357, 364 (1930); **3B**, 130 (1930).

[83] B. Rassow and R. Lüde, *Z. angew. Chem.*, **44**, 827 (1931).

[84] K. R. Gray, E. G. King, F. E. Brauns, and H. Hibbert, *Can. J. Research*, **13B**, 35 (1935).

[85] W. Fuchs, *Ber.*, **62B**, 2125 (1929).

[86] H. Hibbert and J. B. Phillips, *Can. J. Research*, **3B**, 65 (1930).

[87] F. E. Brauns, *The Chemistry of Lignin*, Academic Press, New York, 1952, p. 70.

[88] J. D. Reid, E. C. Dryden, and S. I. Aronovsky, *Paper Trade J.*, **113**, 27 (Aug. 14, 1941).

[89] O. Engel and E. Wedekind, German Patent 581,806 (Aug. 3, 1933); *Chem. Abstracts*, **28**, 1186 (1934); see also K. Storch, *Cellulosechemie*, **17**, 49 (1936).

[90] K. Freudenberg, *Tannin, Cellulose, Lignin*, J. Springer, Berlin, 1933, p. 125.

[91] F. E. Brauns, *The Chemistry of Lignin*, Academic Press, New York, 1952, p. 82.

[92] E. Junker, *Kolloid-Z.*, **95**, 213 (1941).

[93] H. Perrenoud, *Kolloid-Z.*, **107**, 16 (1944).

[94] W. Stumpf and K. Freudenberg, *Angew. Chem.*, **62**, 537 (1950).

Alcohols dissolve only a part of the lignin; phenol, however, in the presence of 0.2% hydrogen chloride at 90–100° C. for 0.5 to 1 hr., dissolves the lignin almost quantitatively, a relatively large amount of phenol condensing with the lignin and giving phenol lignin.[95–98] Unfortunately, the remaining carbohydrates containing most of the cellulose and part of the hemicelluloses are considerably degraded, as shown by their low viscosity, probably through the effect of the hydrochloric acid. The lignin is separated by distilling the major part of the phenol from the filtered solution and triturating the residue with water. The mechanism of the reaction between lignin and phenol is still unknown.

Instead of alcohols, thioalcohols or mercaptans may be used in the presence of a small amount of hydrogen chloride, but the reaction is different since more mercapto groups enter the lignin building unit.[99–101] Of these mercapto compounds, thioglycolic acid[99,100] has probably been most frequently used. Cellulose isolated from wood by means of thio compounds is very light colored, but thus far this method for its isolation has had no commercial use.

Recently, the separation of lignin from cellulose by means of hydrotropic solutions of sodium xylenesulfonate and similar compounds has been recommended, but, because of the concentrated solutions (40–50%) and the high temperature (170–180° C.) required, the cellulose obtained is of poor quality, and the lignin undergoes deep-seated, uncontrollable changes.[102]

(b) PULPING PROCESSES

The isolation of lignin with inorganic reagents involves the methods used for the commercial production of wood cellulose. Because these processes are discussed in detail in Chapter VI-A, only the mechanisms of the reactions between the reagents and the lignin, and the isolation of the lignin preparations obtained will be discussed here. There are three principal pulping processes: the sulfite, the sulfate or kraft, and the soda or alkali. In all three the lignin is obtained as a water-soluble or dilute alkali-soluble lignin derivative.

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[95] L. Kalb and V. Scholler, *Cellulosechemie*, **4**, 37 (1923).

[96] A. Hillmer, *Cellulosechemie*, **6**, 169 (1925).

[97] E. Wedekind, O. Engel, K. Storch, and L. Tauber, *Cellulosechemie*, **12**, 168 (1931).

[98] I. K. Buckland, F. E. Brauns, and H. Hibbert, *Can. J. Research*, **13B**, 61 (1935).

[99] B. Holmberg, *Ing. Vetenskaps Akad., Handl.*, No. **103** (1930); No. **131** (1934).

[100] C. E. Ahlm and F. E. Brauns, *J. Am. Chem. Soc.*, **61**, 277 (1939).

[101] F. E. Brauns and M. A. Buchanan, *Paper Trade J.*, **122**, 49 (May 23, 1946).

[102] R. H. McKee, *Ind. Eng. Chem.*, **38**, 382 (1946).

(*1*) *Lignosulfonic Acid*

In the sulfite process, the lignin is rendered soluble by digesting wood chips with a calcium, magnesium, sodium, or ammonium bisulfite liquor containing an excess of free sulfur dioxide, at an elevated temperature (125–140°C.) for several hours, depending upon the type of pulp desired. During this cook the lignin is converted into a water-soluble salt of lignosulfonic acid and is obtained, together with a small amount of hydrolyzed carbohydrates, in the spent sulfite liquor. From this solution, which contains about 10–12% solids, the sulfonated lignin can be isolated by various methods. These generally consist of a precipitation of the lignosulfonate by salting it out with sodium chloride,[103,104] calcium chloride,[105] mineral acid,[106] or hydrosilicofluoric acid[107]; by precipitating it with limewater, whereby water-insoluble basic calcium lignosulfonate[108] is obtained, or with basic lead acetate as basic lead salt[109]; or by precipitating it with organic bases, such as 1-naphthylamine, quinoline, bis(*N*-dimethylaminodiphenyl)-methane and alkaloids.[110–113] The precipitation of lignosulfonic acid with limewater or basic lead acetate is almost quantitative but in the salting out method only the high-molecular or α-lignosulfonic acids are precipitated; with organic bases, fractions of various molecular sizes of lignosulfonic acids can be obtained, depending upon the base used, thus allowing a fractional separation.[113] By decomposition of the precipitate with alkali, followed by dialysis, a fairly pure lignosulfonic acid can be obtained. Because free lignosulfonic acid is quite unstable in the solid state, its salts are generally used for scientific research and technical application.

The actual mechanism of the reaction taking place in the sulfite cooking process is not yet definitely known. According to Klason,[105] technical spent sulfite liquor contains two types of lignosulfonic acids. They are separated by means of 2-naphthylamine which precipitates the α-acid, leaving the β-acid in solution from which it can be isolated with basic lead acetate. The ratio of the two lignosulfonic acids is about 2:1 but changes

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[103] K. H. A. Melander, *Cellulosechemie*, **2**, 41 (1921).

[104] W. Nippe and A. Ogait, *Cellulosechemie*, **11**, 38 (1930).

[105] P. Klason, *Arkiv Kemi, Mineral. Geol.*, **6**, No. 15 (1917).

[106] M. Hönig and J. Spitzer, *Monatsh.*, **39**, 1 (1918).

[107] G. Racky, *Cellulosechemie*, **20**, 22 (1942).

[108] G. C. Howard, *Ind. Eng. Chem.*, **26**, 614 (1934).

[109] E. G. King, F. E. Brauns, and H. Hibbert, *Can. J. Research*, **13B**, 88 (1935).

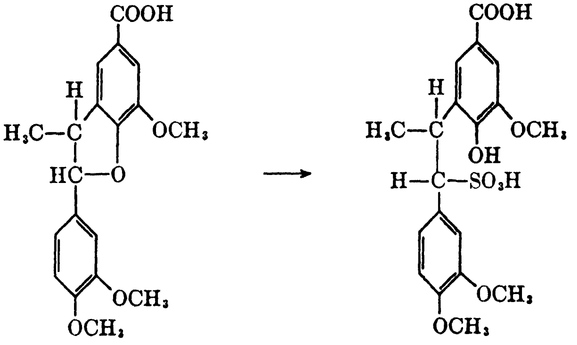
[110] P. Klason, *Ber.*, **53B**, 705, 1862, 1864 (1920).

[111] K. Freudenberg, F. Sohns, and A. Janson, *Ann.*, **518**, 62 (1935).

[112] W. Nippe, *Ber.*, **69B**, 1239 (1936).

[113] H. Erdtman, *Svensk Papperstidn.*, **45**, 315 (1942); *Tappi*, **32**, 346 (1949).

with the cooking conditions. A spent liquor from an experimental cook carried out under mild conditions contains very little or no β-acid,[111] which, according to Hägglund,[114] is formed from the α-acid by further action of the bisulfite. The dissolution of lignin takes place in two stages: in the first, the lignin is sulfonated with the formation of a solid lignosulfonic acid[115] which, in the second step, is rendered soluble by an acid hydrolysis.[116] Several theories have been suggested for the sulfonation of protolignin but most of them have been found to be untenable. Among the more recent ones, Freudenberg[117] has suggested, on the basis of results obtained from model experiments with Erdtman's acid (I), that sulfonation may take place, at least in part, by the opening of an oxygen ring of the furan or pyran type (Formula I) which would lead to the formation of a new phenolic hydroxyl group, as in Formula II. The similarity of the ultraviolet absorption spectrum of a purified lignosulfonic acid to that of isolated native lignin (see Fig. 11), however, indicates that no deep-seated change takes place in the structure of the lignin molecule on sulfonation. Since the number of methoxyl and hydroxyl groups in the lignin is unchanged after sulfona-



I
Erdtman's acid

II
5-{β-[α-(3,4-dimethoxphenyl)]-α-sulfonylpropyl}-4-hydroxy-3-methoxybenzoic acid

[114] E. Hägglund, *Svensk Kem. Tid.*, **42**, 159 (1930).

[115] E. Hägglund, *Svensk Kem. Tid.*, **37**, 116 (1925); **38**, 177 (1926); E. Hägglund and T. Johnson, *Biochem. Z.*, **250**, 221 (1932).

[116] C. Kullgren and C. Du Rietz, *Svensk Kem. Tid.*, **42**, 179 (1930); **43**, 99, 161 (1931); **44**, 15 (1932); **45**, 185 (1933); **46**, 136 (1934); **49**, 52 (1937).

[117] K. Freudenberg, M. Meister, and E. Flickinger, *Ber.*, **70B**, 500 (1937).

tion,[49,109,118,119] this theory seems improbable. On the basis of model experiments by Holmberg,[120] Erdtman,[121–124] on the other hand, believes that he has obtained evidence that the sulfonation occurs by a replacement of hydroxyl groups by sulfonic acid groups because he has found that the more highly lignin has been sulfonated, the lower is its hydroxyl content. When sprucewood is methylated with diazomethane until the methoxyl content of the lignin is 21% and is then subjected to a sulfite cook, the lignin is partly sulfonated but is not dissolved.[26,119] Isolated native spruce lignin, which is completely soluble in bisulfite, has the same methoxyl content when methylated with diazomethane as the lignin in the methylated wood and is also rendered insoluble in bisulfite.[17] In the methylated lignin, which, like the methylated wood, no longer gives the color reaction with Wiesner reagent, the enolized carbonyl group is methylated, indicating that this group plays an important role in the sulfonation and in the color reaction of the lignin.[17] The lowest sulfur content required to bring about a dissolution of the lignin seems to be 3.5%, corresponding to one sulfonic acid group per lignin building unit.[17,49] Because the residual lignin in a sulfite pulp is also sulfonated, it is converted upon chlorination or oxidation (bleaching) into water-soluble decomposition products which make a sulfite pulp more easily bleachable than a soda or kraft pulp. The sulfonation of the residual lignin in pulps also affects the lignin determination in sulfite pulps because part of the lignin is rendered soluble during the treatment with strong mineral acid.

(2) *Thiolignin*

In the sulfate or kraft pulping process, the lignin is rendered soluble by digesting wood chips at 160–180°C. with a mixture of one part of sodium sulfide and two parts of sodium hydroxide as a 5% solution. From the kraft black liquor the lignin, together with some hemicellulose, is precipitated by acidification with mineral acid. After purification the lignin is obtained as a light brown powder, consisting of a mixture of thiolignin and alkali

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[118] E. Hägglund and G. E. Carlsson, *Biochem. Z.*, **257**, 467 (1935).

[119] E. Hägglund, *Holzchemie*, Akadem. Verlagsgesellschaft, Leipzig, 1939, p. 148.

[120] B. Holmberg, *Svensk Kem. Tid.*, **48**, 207 (1936); *Svensk Papperstidn.*, **39**, Special No., 113, 117 (1936).

[121] H. Erdtman, G. Aulin-Erdtman, and B. O. Lindgren, *Svensk Papperstidn.*, **49**, 199 (1946).

[122] H. Erdtman, B. O. Lindgren, and T. Pettersson, *Acta Chem. Scand.*, **4**, 228 (1950).

[123] H. Erdtman, *Research* (London), **3**, 63 (1950).

[124] H. Erdtman and T. Pettersson, *Acta Chem. Scand.*, **4**, 971 (1950).

lignin,[44,125–131] the ratio of which depends upon the sulfidity of the cooking liquor. Although the exact mechanism of the reaction between the sodium sulfide and the lignin is still unknown, there is little doubt that the former reacts with the latter by the introduction of sulfur into the lignin molecule, very probably with the formation of a mercapto group.[44,130]

(3) *Alkali Lignin*

The soda pulping process is carried out in a way very similar to that of the kraft process, the only difference being that, in the former, sodium hydroxide is the sole reagent. It is probable that the reaction mechanism here is the same as that in the kraft process except that oxygen takes the place of sulfur. The alkali lignin obtained on acidification of the soda black liquor varies with the cooking conditions.[132–134] In the kraft and soda pulps also, the residual lignin is changed as is shown by the presence of sulfur in the lignin of the unbleached kraft pulps.[44] For this reason, an alkali-pretreated wood can no longer be delignified by the sulfite process, whereas a wood precooked by a mild sulfite treatment can be further pulped by an alkali cook. Unlike calcium lignosulfonate, both thiolignin and alkali lignin are insoluble in water and are precipitated from their alkaline solutions on acidification. Their calcium salts are also insoluble in water and are precipitated from their alkali salt solutions by calcium ions. This fact accounts, in part, for the difficulty encountered in the bleaching of the pulps with calcium hypochlorite.

3. Structure of Lignin

(a) ELEMENTARY COMPOSITION

The elementary composition of lignin varies with its origin and the method of its isolation. Isolated native spruce lignin has 63.5% carbon and

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[125] P. Klason and B. Segerfelt, *Arkiv Kemi, Mineral. Geol.*, **4**, No. 20 (1913).

[126] B. Holmberg and O. Anderzén, *Ber.*, **56B**, 2044 (1923).

[127] E. Hägglund, *Holz Roh- u. Werkstoff*, **4**, 233 (1941).

[128] T. Enqvist, M. Moilanen, and B. Alfredsson, *Svensk Papperstidn.*, **52**, 517 (1949).

[129] T. Enqvist and E. Hägglund, *Svensk Papperstidn.*, **53**, 85 (1950).

[130] F. N. Lahey and J. W. T. Merewether, *Australian J. Sci. Research*, **A1**, 112 (1948); J. W. T. Merewether, *Australian J. Sci. Research*, **A1**, 241 (1948).

[131] K. Ueno, *J. Japan. Tech. Assoc. Pulp Paper Ind.*, **3**, No. 6, 10, 50 (Nov., 1949).

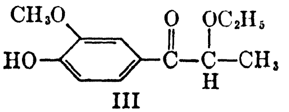
[132] B. Holmberg and J. Wintzell, *Ber.*, **54B**, 2417 (1921).

[133] H. B. Marshall, F. E. Brauns, and H. Hibbert, *Can. J. Research*, **13B**, 103 (1935).

[134] J. W. T. Merewether, *Australian J. Sci. Research*, **A2**, 117, 600 (1949).

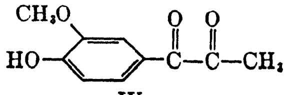
6.1% hydrogen[19]; for other lignin preparations, these figures vary between 62.4 and 64.5% and 5.4 and 6.2%, respectively.[135]

The elucidation of the chemical nature of lignin is considerably more difficult than that of cellulose. Whereas, like cellulose, lignin cannot be isolated in an unchanged state, the former is readily quantitatively hydrolyzed to glucose (see Chapter III-B); lignin cannot be degraded in this way to well-defined simple compounds. The lignin chemist is therefore forced to use as a starting material a product which has already been changed in an unknown manner; moreover, he has to apply methods of degradation which are mostly very drastic and lead to products which may still have the carbon structure of the lignin building stone but which have been changed to such an extent that they no longer permit any conclusions to be drawn as to the original mode of combination. The method that has been applied so successfully to the elucidation of the anhydroglucose units in cellobiose, cellulose, and other polysaccharides cannot yet be applied to lignin because, thus far, it has been impossible to degrade a fully methylated lignin to simple methylated lignin building stones. It is true that, upon ethanolysis of wood, Hibbert and coworkers[136] obtained small amounts of phenylpropane derivatives, some of which contained ethoxyl groups, indicating that the ethyl alcohol had reacted with the lignin building stone. However, the question of whether these simple derivatives, which have been obtained only in a relatively small yield, are actually lignin degradation products or whether they originate from other wood constituents is still open to discussion. If, for example, β-ethoxypropioguaiacone (III) is actually derived from lignin and no rearrangement has occurred in the side chain, then it may be concluded that the β-hydroxyl group is involved in the linkage with another building stone and that a terminal CH_3C— group occurs in the lignin molecule. On the other hand, the isolation of methyl guaiacyl diketone (IV) indicates that rearrangements in the side chain take place during the



III

β-Ethoxypropioguaiacone



IV

Methyl guaiacyl diketone

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[135] F. E. Brauns, *The Chemistry of Lignin*, Academic Press, New York, 1952, pp. 236–242.

[136] H. Hibbert and coworkers, *J. Am. Chem. Soc.*, **61**, 509, 516, 686, 2198 (1939); **62**, 2149, 2803 (1940); **63**, 2371 (1941); **65**, 1176, 1187 (1943); **66**, 39 (1944).

ethanolysis, since it is very doubtful that an α,β-diketo group is present in the lignin molecule.

There is no doubt, however, that the lignin in a coniferous wood differs from that in a deciduous wood. This is shown by the higher methoxyl content of the lignin in the latter because of the presence of the syringyl group (as in XIV) in addition to vanillin (XIII); only the latter is present in lignin from coniferous woods (discussed later). Up to the present time, by determining the number and type of functional groups and by calculating the smallest molecular unit which would permit an integral number of these groups, there appears to be definite evidence for such a building unit of a molecular weight of about 840 and having one enolic and one phenolic hydroxyl group.[66] This unit may be considered to be a multiple of Freudenberg's phenylpropane building stone [137] in the same sense that glucose is the building stone of cellobiose and maltose and the latter are the building units for cellulose and starch, respectively (see Chapter III-B). A lignin building unit of this size is in agreement with many experimental results and has been found to be useful as an aid in considering the relationship between the fundamental groups in lignin; its use in the following discussion is therefore justifiable, although a final decision as to the actual existence of such a building unit must await further confirmation.

(b) AROMATIC NATURE

The high carbon and low hydrogen content of lignin indicate that it is either highly unsaturated or aromatic in character. Although the presence of aliphatic double bonds in lignin is still open to discussion,[3,50,138] there is definite proof that lignin contains aromatic groups. On alkali fusion of spruce lignin, pyrocatechol (V) and protocatechuic acid (VI) are formed, in addition to CO_2 and formic, acetic, and oxalic acids.[46,139] Lignin from beech and other deciduous woods, under the same conditions gives protocatechuic acid and gallic acid (VII).[47] When spruce lignin is treated with sodium hydroxide under somewhat milder conditions, (165–170°C.), and the mixture is methylated with dimethyl sulfate and oxidized with potassium permanganate, veratric acid (VIII), isohemipinic acid (IX),[140] metahemipinic acid (X),[141] dehydrodiveratric acid (XI), and

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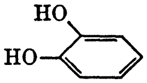
[137] K. Freudenberg, *Tannin, Cellulose, Lignin,* J. Springer, Berlin, 1933, p. 119.

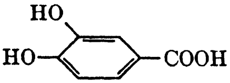
[138] H. Hibbert and R. G. D. Moore, *Can. J. Research,* **14B,** 404 (1936).

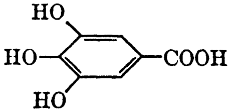
[139] E. Heuser and A. Winsvold, *Cellulosechemie,* **2,** 113 (1921); **4,** 49, 62 (1923); *Ber.,* **56B,** 902 (1932).

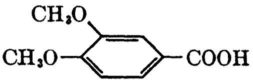
[140] K. Freudenberg, A. Janson, E. Knopf, and A. Haag, *Ber.,* **69B,** 1415 (1936).

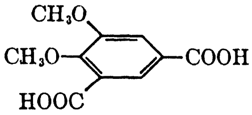
[141] H. Richtzenhain, *Acta Chem. Scand.,* **4,** 589 (1950).

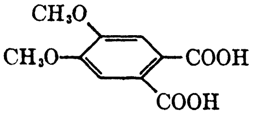

V
Pyrocatechol

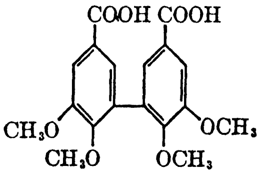

VI
Protocatechuic acid

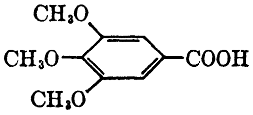

VII
Gallic acid

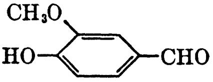

VIII
Veratric acid

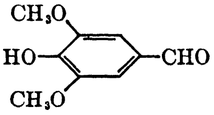

IX
Isohemipinic acid


X
Metahemipinic acid


XI
Dehydrodiveratric acid


XII
Trimethylgallic acid


XIII
Vanillin


XIV
Syringaldehyde

traces of trimethylgallic acid (XII) are obtained.[140] Alkaline hydrolysis of lignosulfonic acid at 160°C. gives vanillin (XIII), acetovanillone, and formaldehyde.[142–146] Alkaline oxidation of spruce lignin, spruce lignosulfonic

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[142] K. Kürschner and W. Schramek, *Technol. u. Chem. Papier- u. Zellstoff-Fabr.*, **28**, 65 (1931); **29**, 35 (1932).

[143] G. H. Tomlinson and H. Hibbert, *J. Am. Chem. Soc.*, **58**, 345, 348 (1936).

[144] E. Hägglund, *Svensk Papperstidn.*, **39**, 347 (1936); E. Hägglund and O. Alvfeldt, *Svensk Papperstidn.*, **40**, 236 (1937).

[145] K. Kratzl, *Monatsh.*, **80**, 271 (1949).

[146] T. Kleinert, *Monatsh.*, **80**, 582 (1949).

acid, and even sprucewood in the presence of nitrobenzene or any other mild oxidation reagent gives up to 25% vanillin (based on the lignin).[147,148] On similar treatments, lignins from deciduous woods give syringaldehyde (XIV) in addition to vanillin.[149] Dry distillation of lignin yields small amounts of eugenol, guaiacol, and vanillic acid.[150]

(c) REACTIVE GROUPS

Lignin contains various characteristic groups. The presence of aromatically combined methoxyl groups has been definitely established.[3,151] Isolated native spruce lignin has a methoxyl content of 14.8%, corresponding to four methoxyl groups per lignin building unit of a molecular weight of about 840[19]; other lignin preparations from coniferous woods possess between 15 and 16.5% methoxyl, depending upon the mode of their isolation; lignins from deciduous woods have a methoxyl content of around 21%.[152] When carefully prepared spruce lignin is subjected to a distillation with 12% hydrochloric acid[46,72,153] or 28% sulfuric acid,[67] up to 2.5% formaldehyde is split off; it originates from the side chain of a phenylpropane building stone.[154–156] Whereas the absence of other types of alkoxyl,[157] carboxyl,[158] and acetyl groups[159] in protolignin has been established, the presence of hydroxyl groups is shown by the fact that such lignin can be acetylated and methylated. The number and type of these groups may vary in lignins from different wood species.[160,161] That at least one of the four hydroxyl groups in the spruce lignin building unit is phenolic is shown

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[147] K. Freudenberg, W. Lautsch, and K. Engler, *Ber.*, **73B**, 167 (1940).

[148] I. A. Pearl, *J. Am. Chem. Soc.*, **64**, 1429 (1942).

[149] R. H. Creighton, J. L. McCarthy, and H. Hibbert, *J. Am. Chem. Soc.*, **63**, 312 (1941).

[150] B. Rassow and P. Zickmann, *J. prakt. Chem.*, **123**, 189 (1929).

[151] P. B. Sarkar, *J. Indian Chem. Soc.*, 12, 542 (1935).

[152] F. E. Brauns, *The Chemistry of Lignin*, Academic Press, New York, 1952, pp. 237–239.

[153] E. Hägglund and coworkers, *Biochem. Z.*, **147**, 74 (1924); **179**, 376 (1927); **207**, 1 (1929).

[154] M. J. Hunter, G. F. Wright, and H. Hibbert, *Ber.*, **71B**, 734 (1938).

[155] K. Freudenberg, F. Klinck, E. Flickinger, and A. Sobek, *Ber.*, **72B**, 217 (1939).

[156] K. Freudenberg and E. Plankenhorn, *Chem. Ber.*, **80B**, 149 (1947).

[157] E. Hägglund and O. Sandelin, *Svensk Kem. Tid.*, **46**, 83 (1934).

[158] E. Hägglund, *Holzchemie*, Akadem. Verlagsgesellschaft, Leipzig, 1939, p. 200

[159] E. F. Kurth and G. J. Ritter, *J. Am. Chem. Soc.*, **56**, 2720 (1934).

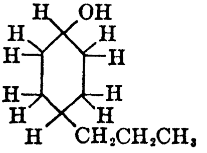
[160] K. Freudenberg and G. Dietrich, *Ann.*, **563**, 146 (1949).

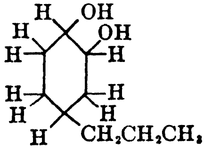
[161] K. Freudenberg and A. Götz, cited in Ref. 160.

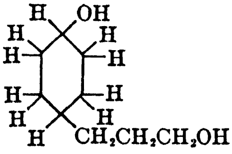
by the solubility of isolated native lignin and its alcohol lignins in dilute sodium hydroxide and their precipitation from these solutions with carbon dioxide.[19,66,84,162] The presence of a phenolic hydroxyl group in a lignosulfonic acid building unit has also been definitely proved.[109] The other OH groups are aliphatic and probably secondary and tertiary in nature.[160,161] Isolated native spruce lignin possesses one readily enolizable carbonyl group per lignin building unit[66]; in the alcohol lignins, it has reacted to form an acetal.[16,19,80] This carbonyl group plays an important role in the sulfonation of lignin and in the color reaction with phloroglucinol and hydrochloric acid.[17,37]

(d) OXIDATION AND HYDROGENATION

Under mild oxidation conditions vanillin is formed; under more drastic conditions lignin is completely converted into water-soluble products, a reaction which is utilized in the bleaching of wood pulps. On oxidation with chromic acid, small amounts of acetic acid are formed which may indicate the presence of a CH_3C— group in the lignin molecule.[49,160,163] Thus far no oxidation product has been isolated from lignin to permit any conclusions to be drawn as to the type of linkage between the single lignin building stones. The same holds true for the results of the reduction of lignin. With hydriodic acid and red phosphorus, hydrochloric acid spruce lignin gives a mixture of hydrocarbons from which no definite compound has been isolated.[69] On catalytic hydrogenation of methanol maple lignin at 250 atmospheres and 250–260°C. in the presence of copper chromite or Raney nickel as a catalyst, 11% of 4-propyl-1-cyclohexanol (XV), 3.2% of 4-propyl-1,2-cyclohexanediol (XVI), and 24% of 4(ω-hydroxypropyl)-1-cyclohexanol (XVII) are obtained in addition to 25% of methanol originating from the methoxyl groups, some water, and a colorless resin of the composition


XV
4-Propyl-1-cyclohexanol


XVI
4-Propyl-1,2-cyclohexanediol


XVII
4-(ω-Hydroxypropyl)-
1-cyclohexanol

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[162] H. Richtzenhain, *Chem. Ber.*, **83B**, 488 (1950).
[163] W. S. MacGregor, T. H. Evans, and H. Hibbert, *J. Am. Chem. Soc.*, **66**, 41 (1944).

$(C_6H_{11}O)_x$.[164–169] These results support the concept that a large part of the lignin molecule is composed of lignin building stones having the phenylpropane skeleton. However, even these results give no clear indication as to how building stones are linked together.

(e) ALKYLATION

Alkylation reactions have often served for the characterization of lignin and its derivatives.[170] Isolated native spruce lignin, when methylated with diazomethane in ether suspension, gives a partly methylated product with 18.3% methoxyl content which, on further methylation in dioxane solution, increases to 21.5%.[17] On methylation of this product with dimethyl sulfate, a fully methylated native spruce lignin with 30.5% methoxyl is obtained.[19] Methylation of hydrochloric acid spruce lignin with diazomethane in ether suspension increases the methoxyl content from 15.5 to 19.8%,[171] whereas in cyclohexanol a methoxyl content of 21.5% is reached.[25] Methylation of hydrochloric acid spruce lignin with dimethyl sulfate and sodium hydroxide gives a fully methylated spruce lignin with 32.4% methoxyl.[25] A fully methylated beech lignin has a methoxyl content of 36.1%.[172] Diazomethane methylation of spruce lignosulfonic acid with a sulfur content of 3.5% leads to a partially methylated product with 19.2% methoxyl[109]; on further methylation with dimethyl sulfate, the methoxyl increases to 27.7%, which is a completely methylated lignosulfonic acid[49,109,173]; this indicates that the number of hydroxyl groups in the lignin molecule has not been changed by the sulfonation.[173]

(f) SUBSTITUTION REACTIONS

Of the halogenation reactions with lignin, chlorination is of technical importance because it is utilized in the multistage bleaching of wood pulp (see Chapter VII), particularly of soda and kraft pulps, and also in the pro-

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[164] E. E. Harris, J. D'Ianni, and H. Adkins, *J. Am. Chem. Soc.*, **60**, 1467 (1938).

[165] H. Adkins, R. L. Frank, and E. S. Bloom, *J. Am. Chem. Soc.*, **63**, 549 (1941).

[166] H. Hibbert and coworkers, *J. Am. Chem. Soc.*, **63**, 3052, 3056, 3061 (1941); **70**, 57, 67 (1948).

[167] J. F. Saeman and E. E. Harris, *J. Am. Chem. Soc.*, **68**, 2507 (1946).

[168] E. E. Harris, J. F. Saeman, and C. B. Bergstrom, *Ind. Eng. Chem.*, **41**, 2063 (1949).

[169] I. T. Clark, J. R. Hicks, and E. E. Harris, *Tappi*, **34**, 6 (1951).

[170] E. Heuser, R. Schmidt, and L. Gunkel, *Cellulosechemie*, **2**, 81 (1921).

[171] K. Freudenberg and H. Hess, *Ann.*, **448**, 133 (1926).

[172] M. A. Buchanan, F. E. Brauns, and R. L. Leaf, Jr., *J. Am. Chem. Soc.*, **71**, 1297 (1949).

[173] E. Hägglund, *Holzchemie*, Akadem. Verlagsgesellschaft, Leipzig, 1939, p. 150.

duction of straw cellulose by the Pomilio and de Vains processes (see Chapters VI-D, VII). From the point of view of science, the chlorination of lignin has not given any results of value because oxidation and substitution in the aromatic ring occur with the simultaneous removal of methoxyl groups.[174] Bromination under carefully controlled conditions results in the substitution of one aromatic hydrogen atom per lignin building stone,[3] whereby at least a part of the bromine is attached to the carbon atom 6 of the benzene ring as is shown by the formation of 6-bromovanillin on alkaline oxidation with nitrobenzene.[175] The presence of aromatic hydrogen atoms capable of being substituted is further shown by the reaction of lignin with mercuric acetate in alcoholic solution, whereby one acetoxymercury group is introduced per lignin building stone.[176,177] That some of these groups are at the carbon atom 5 of the benzene ring is shown by the fact that, when the acetoxymercury group is replaced by iodine and the iodolignin is oxidized, some 5-iodovanillin is obtained.[175]

(g) NATURE OF COMBINATION OF LIGNIN BUILDING STONES

Although research on lignin is as old as that on cellulose, the structure of lignin is still unknown. The main reason for this is that lignin thus far cannot be hydrolyzed to monomeric or oligomeric fragments which would allow conclusions to be drawn as to their exact structure and their combination. However, considerable progress has been made during the past twenty-five years.

Many structural formulas have been proposed for lignin,[178–183] most of them speculative in nature, but only those which are based on sound experimental evidence and which appear to be of most significance will be considered here. As early as 1897, Klason[184] recognized the close relationship between lignin and coniferin (XVIII), the glucoside of coniferyl alcohol, which occurs in the cambial sap of spruce. He suggested that lignin is a condensation or polymerization product of coniferyl or oxyconiferyl al-

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[174] E. Heuser and R. Sieber, *Z. angew. Chem.*, **26**, 801 (1913).

[175] W. Lautsch and G. Piazolo, *Ber.*, **73B**, 317 (1940).

[176] K. Freudenberg and H. F. Müller, *Ber.*, **71B**, 2500 (1938).

[177] K. R. Gray, F. E. Brauns, and H. Hibbert, *Can. J. Research*, **13B**, 48 (1935).

[178] C. F. Cross, E. J. Bevan, and C. Beadle, *Ber.*, **26**, 2520 (1893).

[179] A. G. Green, *Z. Farben- u. Textilchem.*, **3**, 97 (1904).

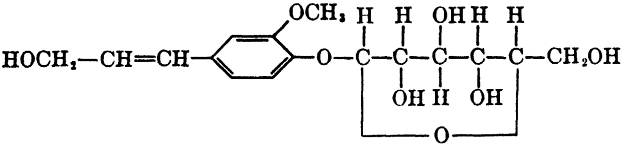
[180] K. Kürschner, *Zur Chemie der Lignin Körper*, F. Enke, Stuttgart, 1925, p. 37.

[181] T. Pavolini, *Industria chimica*, **6**, 1367 (1931).

[182] W. Schrauth, *Z. angew. Chem.*, **36**, 149 (1923).

[183] W. Fuchs, *Z. angew. Chem.*, **44**, 111 (1931).

[184] P. Klason, *Svensk Kem. Tid.*, **9**, 135 (1897).



XVIII

Coniferin (glucoside of coniferyl alcohol)

cohol when he found that such products exhibit properties very similar to those of lignin. Later,[185] he suggested that coniferyl aldehyde may play an important role as a basic building stone for lignin. Klason's concept had a stimulating effect on other lignin chemists who put forward structural formulas consisting of condensed phenylpropane building stones.[186,187]

The first systematic attempts to elucidate the structure of lignin were made in 1929 by Freudenberg and his school[47,140] and, a few years later, by Hibbert and coworkers.[188,189] Basing his conclusions on his experience with other natural products, such as cellulose, polypepsides, and tannins, Freudenberg decided that lignin is a condensation polymer of simple building stones having a phenylpropane structure.[190] Although he realized that the time was still too early to propose a structural formula for lignin, he formulated, as a working hypothesis, "primary lignin" as a linear polymer chain in which the building stones are linked together by an ether bridge between the hydroxyl groups of the terminal carbon atom of the side chain and the *p*-hydroxyl group at the ring of the next building stone.[191] Although such a scheme explains some lignin reactions, it is not in harmony with others, such as the conversion of "primary" into "secondary" (or more highly condensed) lignin and the behavior of lignin toward hydriodic acid.

When a study of the polymerization of coniferyl alcohol, which takes place in the presence of a trace of acid, showed that the alcoholic hydroxyl group is eliminated together with a hydrogen of the nucleus of a second molecule, and when the oxygen content of lignin was taken into consideration, Freudenberg[191,192] arrived at the conclusion that the lignin building stone must be a hydroxylated phenylpropane derivative in which the state of oxidation of the side chain is the same as that in glycerol. The following such derivatives are possible, with R representing the pyrocatechol group:

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[185] P. Klason, *Ber.*, **53B**, 706 (1920).

[186] K. Kürschner, *Zellstoff-Faser*, **32**, 19 (1935).

[187] T. Pavolini, *Industria chimica*, **6**, 1367 (1931).

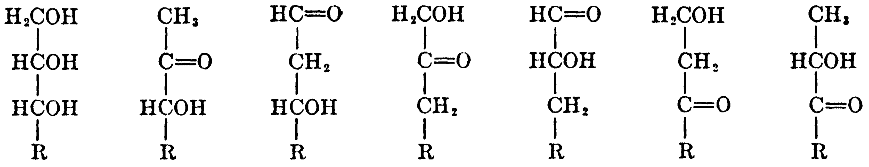
[188] H. Hibbert and H. J. Rowley, *Can. J. Research*, **2**, 357 (1930).

[189] H. Hibbert and F. E. Brauns, *Pulp Paper Can.*, **34**, 187 (1933).

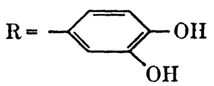
[190] K. Freudenberg, *Tannin, Cellulose, Lignin*, J. Springer, Berlin, 1933, p. 120.

[191] K. Freudenberg, *Tannin, Cellulose, Lignin*, p. 134.

[192] K. Freudenberg and W. Lautsch, *Naturwissenschaften*, **27**, 227 (1939); see also K. Freudenberg, *Ann. Rev. Biochem.*, **8**, 89 (1939); see also H. Hibbert, *J. Am. Chem. Soc.*, **61**, 725 (1939).



$$\begin{array}{ccccccc}
H_2COH & CH_3 & HC{=}O & H_2COH & HC{=}O & H_2COH & CH_3 \\
| & | & | & | & | & | & | \\
HCOH & C{=}O & CH_2 & C{=}O & HCOH & CH_2 & HCOH \\
| & | & | & | & | & | & | \\
HCOH & HCOH & HCOH & CH_2 & CH_2 & C{=}O & C{=}O \\
| & | & | & | & | & | & | \\
R & R & R & R & R & R & R
\end{array}$$



According to Freudenberg, any one of the compounds, e.g., 1-guaiacylglycerol [1-(4-hydroxy-3-methoxyphenyl)-1,2,3-propanetriol] (see p. 504) (XIX), acetylguaiacylcarbinol [acetyl (4-hydroxy-3-methoxyphenyl) methanol or 1-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone] (XX), may react with another in such a way that ether linkages are formed, as in Formulas XXI and XXII. By condensation of several of such building stones larger units are formed, as shown in XXIII and XXIV. Freudenberg further assumed that water is split off between the primary hydroxyl group of the side chain and a hydrogen of the phenyl ring of the next building stone in a way similar to the nuclear condensation of coniferyl alcohol, with the formation of chroman (XXV) or coumaran (XXVI) rings. In softwood only vanillyl or coniferyl groups (as in XVIII) participate in the formation of lignin; in hardwoods, the lignins of which have a higher methoxyl content, some of the lignin building stones have a syringyl group. The fact that spruce lignin gives about 25% vanillin (XIII) indicates that at least one quarter of the lignin building stones must have the vanillyl group arranged in such a way that it can give vanillin on oxidative degradation. This, of course, does not imply that the remaining part does not have the vanillyl grouping. Further support for his theory was obtained by Freudenberg by experiments on the synthesis of ligninlike products by the action of dehydrogenases isolated from the juice of the mushroom *Psalliota campestris* on coniferyl alcohol (XXVII, R = H) whereby products are obtained which in their chemical and physical behavior very closely resemble isolated native spruce lignin.[193,194] Under similar conditions, sinapinyl alco-

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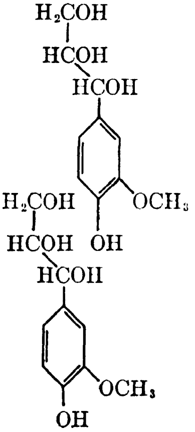
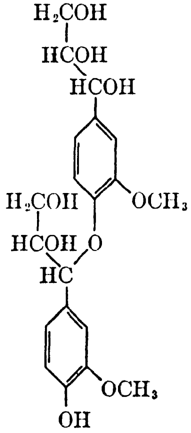
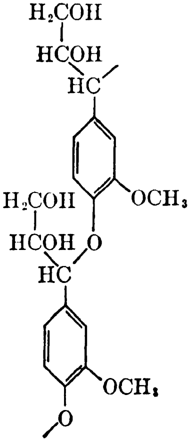
[193] K. Freudenberg, *Sitzber. heidelberg. Akad. Wiss. Math. naturwiss. Klasse,* No. **5**, 151 (1949); K. Freudenberg and W. Heimberger, *Chem. Ber.*, **83**, 519 (1950).

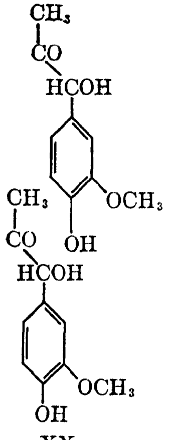
[194] K. Freudenberg and G. Gehrke, *Chem. Ber.*, **84**, 443 (1951); K. Freudenberg, R. Kraft, and W. Heimberger, *Chem. Ber.*, **84**, 472 (1951).

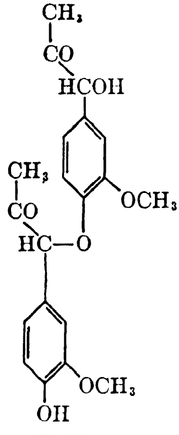
hol (XXVII, $R = CH_3O$), which has the 4-hydroxy-3,5-dimethoxyphenyl grouping (the syringyl analog of coniferyl alcohol), gives an amorphous product with a methoxyl content of 23.2%, which is higher than that found

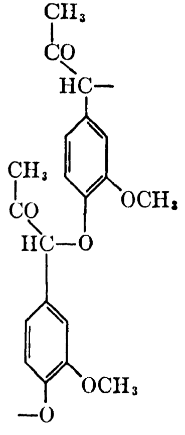

XIX


XXI

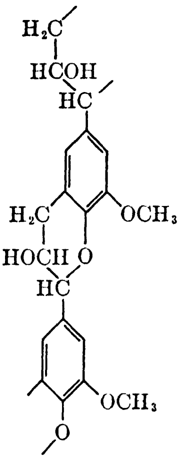

XXIII


XX

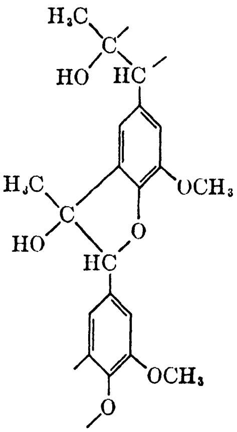

XXII


XXIV

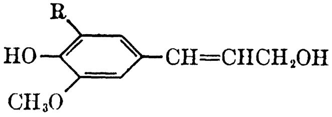
for isolated native aspen lignin.[172] It must be remembered, however, that this "synthetic lignin" is formed exclusively from a dimethoxy derivative, whereas lignins from deciduous woods are either a mixture of what might be called vanillyl-type and syringyl-type lignins or a copolymer of vanillyl-type and syringyl-type lignin building stones. Lignin from coniferous woods is



XXV



XXVI



XXVII
Sinapinyl alcohol (R = CH_3O)

built up only from the vanillyl-type building stones. A claim by Russell[195] that he had synthesized poly-8-methoxydihydrobenzopyrone and that it was identical with gymnosperm lignin was found to be erroneous.[196]

The discovery by Hibbert and coworkers[197–199] of small quantities of guaiacol and acetovanillone, in addition to vanillin, on alkaline hydrolysis of lignosulfonates from sprucewood, and of pyrogallol 1,3-dimethyl ether, syringaldehyde, and acetosyringone from lignosulfonates from maplewood under the same conditions indicates the presence of phenyl derivatives with side chains of at least two carbon atoms. These two-carbon side chains, of course, may be the result of a degradation of a three-carbon chain originally present. The presence of such a side chain is proved not only by the formation of substantial amounts of cyclohexylpropane derivatives on hydrogenolysis of lignin but also by the isolation of phenylpropane derivatives[200] from the aqueous solution of the alcoholysis products of wood. In the preparation of alcohol lignins, such as methanol, ethanol, and glycol lignins from spruce and maplewood, a considerable amount of the dissolved lignin is not precipitated from the alcoholic solution by the addition of water but remains in the aqueous mother liquor as so-called "water-soluble lignin."[66,84]

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[195] A. Russell, *J. Am. Chem. Soc.*, **70**, 1060, 2864 (1948); A. Russell, J. H. Baity, and H. E. Smith, *J. Am. Chem. Soc.*, **71**, 956 (1949).

[196] H. E. Smith, C. R. Russell, and L. E. Schniepp, *J. Am. Chem. Soc.*, **73**, 793 (1951).

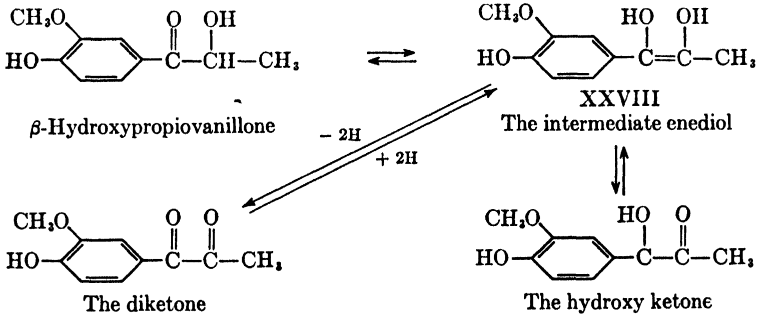
[197] F. Leger and H. Hibbert, *Can. J. Research*, **16B**, 68 (1938); *J. Am. Chem. Soc.*, **60**, 565 (1938).

[198] I. K. Buckland, G. H. Tomlinson, and H. Hibbert, *J. Am. Chem. Soc.*, **59**, 597 (1937).

[199] A. Bell, W. L. Hawkins, G. F. Wright, and H. Hibbert, *J. Am. Chem. Soc.*, **59**, 598 (1937).

An investigation of the aqueous solution from the ethanolysis of maplewood revealed the presence of syringaldehyde, methyl vanilloyl ketone, methyl syringoyl ketone, β-ethoxypropiovanillone, and β-ethoxypropiosyringone. Because ethoxy groups are absent from native lignin, their presence in the ethoxy compounds must be the result of an ethylation of the corresponding hydroxyl groups which may either be free in the protolignin or be set free by an alcoholic cleavage of an ether linkage. All these compounds are related to the various types of lignin building stones suggested by Freudenberg and add experimental support to his concept regarding their structure. Unfortunately, the isolation of these alcoholysis products gives no indication as to the type of condensation of the building stones in the polymeric lignin molecule, although it is possible that the β-hydroxyl group in the side chain is involved.

According to Hibbert,[201] the polymerization of lignin building stones takes place as follows: β-hydroxypropiovanillone and β-hydroxypropiosyringone are very labile compounds and, under the effect even of mild reagents, undergo intramolecular dismutation transformations involving



β-Hydroxypropiovanillone

XXVIII
The intermediate enediol

The diketone

The hydroxy ketone

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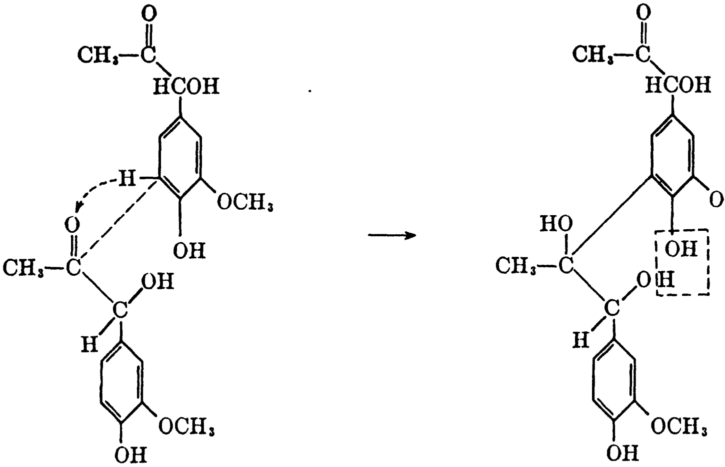
[200] H. Hibbert and coworkers, *J. Am. Chem. Soc.*, **60**, 2815 (1938); **61**, 509, 516, 2198 (1939); **62**, 2803 (1940).

[201] H. Hibbert, *Paper Trade J.*, **113**, 35 (July 24, 1941); *Ann. Rev. Biochem.*, **11**, 183 (1942).

hydrogen migration and oxidation-reduction systems with an enediol (XXVIII) as an intermediate product. Compounds of this type, having a phenyl and a carbonyl group or two hydroxyl groups at two neighboring carbon atoms linked by a double bond, have a strong tendency to undergo nuclear condensation with the formation of dimeric and polymeric products.



XXIX XXX

Such a type of condensation is shown in Formulas XXIX and XXX. Heterocyclic rings of a hydrofuran type, similar to that suggested by Freudenberg, are formed in such a reaction. The two condensation mechanisms differ only in the order in which the various steps are assumed to take place. With the syringyl group present, no nuclear condensation can occur because both positions ortho to the hydroxyl groups are occupied by methoxyl groups. Lignin from deciduous woods, with its relatively high content of sinapinyl building stones, therefore seems to be less highly condensed and to have a lower molecular weight than that from coniferous woods.

The foregoing discussion of the chemistry of lignin may be summarized briefly as follows. At the present time no clear-cut picture of the structure of the lignin molecule can be presented. There is, however, substantial evidence that lignin is built up, to a large extent, of phenylpropane building stones having either free or masked phenolic hydroxyl groups in the para position and methoxyl groups in the meta position to the side chain. Whether these building stones are uniform or differ in their degree of oxidation in the side chain and whether they are linked together according to a single pattern or are condensed in various ways as suggested by Freudenberg are still open questions. The fact that in the sinapinyl group a methoxyl group is attached to the carbon atom 5 of the benzene ring prevents nuclear condensation such as has been assumed to occur in the lignin from deciduous woods. If it is assumed that lignin is a long-chain condensation or polymerization product of simple building stones, any attempt by the lignin chemist to elucidate the molecular structure of lignin has to include its degradation in such a way that dimeric or oligomeric fragments are obtained with the original linkage between the building stones preserved.[202,203] Further decomposition of these fragments, after all their functional groups have been established and if possible stabilized, should provide evidence as to the mode of linkage of the building stones. This method is similar to that which has been applied so successfully to the elucidation of the structure of cellulose by its degradation to cellobiose and oligosaccharides from which, in turn, the mode of polymerization has been established (see Chapter III-B).

4. Nature of the Other Noncarbohydrate Constituents of Wood and Straw

In addition to lignin there are other noncarbohydrate constituents of wood and straw, but only in minor amounts. In wood they consist of resins, tannins, fats, waxes, some coloring matter, proteins, and mineral compounds; in straw and other annual plants they are chiefly proteins and inorganic matter. The amount of these components in woods varies widely with the species.

The resins consist of resin acids, resin alcohols, and resenes. The amount of resins in coniferous woods varies from 2.3 to 25%, that in deciduous woods from 0.7 to 3%; they have an unfavorable effect upon the pulping properties of the wood in the sulfite process, causing "pitch trouble." Woods, such as pine, which are high in resin content, are generally pulped by the kraft process (see Chapter VI-A). The resins are then recovered in the tall oil.[204] When the wood is seasoned before being pulped, the resins are changed, thus reducing the pitch trouble.

The tannin content of woods also varies widely with the species. In the coniferous woods, tannins are located chiefly in the bark—for instance, the barks of western larch, western yellow pine, and hemlock contain 10.6–10.9%, whereas the woods contain 6.7, 8.9, and 1%, respectively.[205] There

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[202] C. Gustafsson, K. Sarkanen, S. Kahila, and E. Niskasaari, *Paper and Timber (Finland)*, **33**, 74 (1951).

[203] F. E. Brauns, *Fortschr. Chem. org. Naturstoffe*, **5**, 225 (1948).

[204] G. C. Harris, *Tappi Monograph Series*, No. **6**, 167 (1948).

[205] H. K. Benson and F. M. Jones, *Ind. Eng. Chem.*, **9**, 1096 (1917).

are two types of tannins: the depsides or polyesters, which are hydrolyzable; and the catechol tannins or phlobatannins, condensation products with building stones joined by carbon-to-carbon linkages, which cannot be split by hydrolysis. These tannins are mostly soluble in water but decompose when heated with mineral acids; the phlobatannins, when treated in this way, give red precipitates known as phlobaphenes. The tannins that are not changed during the pulping process are removed with the spent liquor. There may exist a relationship between the nonhydrolyzable tannins and lignin. The lignans such as pinoresinol, lariciresinol, conidendrin (also known as sulfite liquor lactone), and hinokinen are dimeric condensation products of phenylpropane building stones, often having a methoxyl group in the meta position and a hydroxyl group in the para position to the side chain. They are crystalline compounds, soluble in organic solvents. It has been claimed that they interfere in the bisulfite cooking process by preventing a complete pulping,[206] because these phenolic compounds condense with the lignin and render it insoluble in the bisulfite solution.

The dye pigment content of woods usually used by the pulp industry is very low; it consists mostly of glucosides of phenolic compounds, such as flavones and anthocyanins, and may be related to lignin. Because natural dyestuffs are soluble in alkali they are removed in the alkaline pulping processes. In the bisulfite process, however, they remain in the pulp and may affect its color.

The proteins and mineral components in woods amount to 1.3 and 0.4—1.1%, respectively, and have no effect on the pulping process. The high content of silica prevents straws from being pulped by the bisulfite process.[207]

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[206] H. Erdtman, *Svensk Papperstidn.*, **42**, 115 (1939); *Tappi*, **32**, 303 (1949); H. Erdtman, A. Frank, and G. Lindstedt, *Svensk Papperstidn.*, **54**, 275 (1951).

[207] S. I. Aronovsky, A. J. Ernst, H. M. Sutcliffe, and G. H. Nelson, *Paper Trade J.*, **126**, 78 (June 24, 1948).